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OF THE

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NOTE.

The publications of the Academy in octavo form, called "Proceedings," were begun in 1846, by Dr. Asa Gray, then Corresponding Secretary. The original plan was to print with the proceedings of the meetings of the Society abstracts of the papers presented, reserving the more formal finished papers for the quarto publications, called "Memoirs." This practice was continued until 1873, by Professors W. B. Rogers and Joseph Lovering, who succeeded Dr. Gray in the same office, and during these twenty-seven years eight volumes were published. Meantime, on account of the difficulty of procuring abstracts, that feature of the plan fell into disuse; while the greater convenience of the octavo form for most scientific subjects, as well as its greater economy, led to the printing of papers *in extenso* amidst the proceedings of the meetings. For this reason, the undersigned, on assuming the direction of the Academy's publications, in 1873, published the scientific papers separately, under appropriate captions, and made the proceedings of the meetings an appendix to the papers; and during the nineteen years he has held the office of Corresponding Secretary an octavo volume thus made up has been published each year.

The original idea of incorporating with the proceedings of the meetings such brief abstracts of verbal communications as may be furnished by the authors was an excellent one; and although latterly the plan has been seldom followed, it has been by no means abandoned. It should be borne in mind by members that this method of partial publication is still practicable, and may be very useful for preliminary notices during an extended investigation.

JOSIAH P. COOKE,
Editor Vols. IX. to XXVII. inclusive.

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PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XXVII.

PAPERS READ BEFORE THE ACADEMY.

I.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXVII. — SOME CONSIDERATIONS REGARDING HELMHOLTZ'S THEORY OF CONSONANCE.

BY CHARLES R. CROSS AND HARRY M. GOODWIN.

Presented June 10, 1891.

THE present paper contains the results of a number of experiments relating to certain aspects of the theory of consonance and dissonance put forth by Helmholtz in the *Tonempfindungen.* In that work the author gives as the number of beats producing the maximum of harshness from thirty to forty per second, reaching this conclusion from a consideration of the amount of dissonance of various different chords in different octaves.

Mayer * studied the relation of the number of beats causing the greatest harshness to the absolute pitch, and showed that there is a marked rise in this number as the pitch becomes higher. The beats studied by Mayer, however, as he himself pointed out, are in several respects different from those which occur in the case of mistuned unisons. They were caused by rotating a disk, which was provided with a circle of holes near the circumference, between a vibrating tuning-fork and a resonator, the number of beats per second being of course greater as the speed of the disk was greater. Hence the sound-wave reaching the ear was not at all a compound wave due to the superposition on one another of two simple sound-waves slightly differing in length, as in ordinary beats, but merely a series of simple waves with gaps, as it were; while the passage from maximum to minimum intensity in the sound reaching the ear was very different in its character from that actually occurring with ordinary beats. In referring to such beats as those studied by Mayer, we shall for the sake of brevity designate them as "interruptional beats," and the ordinary beats we shall call "interference beats."

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* American Journal of Science, Vol. CVIII. p. 241; Vol. CIX. p. 267.

We have thought it desirable to ascertain what results would be reached in different registers with interference beats, such as are present in actual dissonances. It was of course necessary to employ simple tones. Our method was a direct one, viz. to produce two such tones simultaneously, and to vary the pitch of one of these by known amounts, estimating by the ear when the sound became the harshest.

As a source of sound we employed the cylindrical resonators of Koenig, which were sounded by gently blowing across the opening a stream of air from the brass, slit-shaped "universal embouchure" made by the same maker. We found these tones to be very pure and loud, while their pitch could be varied with great readiness without altering the intensity of the sound emitted. The set of resonators employed ranged from Sol_1 to Mi_5, the ranges of successive resonators overlapping slightly. The two embouchures were connected to a Y by rubber tubes, and placed on adjustable supports in suitable relation to the apertures of the two resonators to be sounded. The strength of the blast was regulated by a stopcock, and the bore of each rubber tube could be closed more or less by a clamp, so that the force of the jet of air at each resonator could be adjusted with all needed delicacy. Thus the intensity of the notes given out by the two resonators could be adjusted so that they were exactly equal in loudness. This was done by causing the tones to beat slowly, and so adjusting the apparatus that there was apparently an absolute silence when the sound fell to its minimum intensity. No difficulty was found from any whirring of the sheet of air as it struck the edges of the aperture, since by proper adjustment this could be made quite inappreciable. Having once made the necessary adjustments, the pitch of either note could be varied by drawing out or pushing in the lower half of the resonator. The actual pitch of the note given by the resonator was in all cases determined by comparison with a tuning-fork of known rate. As the pitch of the resonator when blown is to a certain extent dependent on the position of the embouchure and the strength of the blast, it would not be safe to assume that the actual note given by the resonator was that marked upon it. Neither resonator when sounded sensibly affected the pitch of the note given by the other.

The determination of the point at which the harshness of the dissonance produced by the tones of the two resonators reaches a maximum is of course a very difficult problem to be solved exactly. It is, moreover, a question still to be investigated, whether precisely the same results would be reached by different observers possessed of equally good perception. The following figures given in Table I. were ascertained from a long series of observations by one of the writers (Mr. Goodwin). They are liable to an error of a single beat in either direction, possibly somewhat more in one or two cases. They furnish, however, the first series of direct measurements of this kind which we know.

TABLE I.

Ut_2	Ut_3	Sol_3	Ut_4	Sol_4	Ut_5	Mi_5
19	26	29	32	36	41	45

It will be noticed that the result for Ut_4, 32 beats per second, agrees very closely with the number 33, which Helmholtz gives for maximum dissonance in the middle registers. He found that of the ordinary musical intervals, $b' \; c''$, as he designates it, was the most dissonant, and as this gave 33 beats per second he considered this number as giving the harshest effect for tones of corresponding pitch.

The notes furnished by the resonators are also well adapted for the direct study of the limit at which the beats cease to be audible when their number is increased. As the interval between the beating notes is increased, the beats heard become fainter and fainter until they disappear. It is all but impossible to fix upon the precise point of disappearance, since the change in loudness of the beats is so gradual. But, as will presently appear, our results clearly show that the maximum number of beats perceptible, like the number giving the maximum dissonance, varies greatly with the pitch of the notes sounded.

The pitch of one of the resonators was varied so as to run upward and downward through the vanishing point of the beats. This procedure was extremely tiresome, and the values obtained were found to be considerably influenced by fatigue of the ear. The following table (Table II.) gives the results obtained when the ear was in good condition. The first column gives the rate of vibration of the lower note, the next four the rate of the upper note as found in corresponding series of observations; the seventh column gives the number of beats, and the last the interval between the two notes.

TABLE II.

Lower Note.	Upper Note.				Mean.	Beats.	Interval.
	1.	2.	3.	4.			
Ut_2 128	175	170	177	173	174	46	Fourth +.
Ut_3 256	328	321	326	329	326	70	Major third +.
Sol_3 384	467	458	469	460	464	80	Major third − 16 vibrations.
Ut_4 512	620	616	618	611	616	104	Minor third (nearly).
Sol_4 768	882	890	886	890	887	119	Tone + ¼ tone (nearly).
Ut_5 1024	1160	1167	1160	1163	1163	139	Tone + 11 vibrations.
Mi_5 1280	1420	1424	1421	1418	1420	140	Tone − ⅛ tone (nearly).

These figures abundantly confirm for interference beats the results already reached by Mayer for interruptional beats, viz. that the ear is capable of appreciating a greater number of beats as the pitch of the beating notes rises. They also show very beautifully the increasing consonance of small intervals as the pitch rises, noted by Helmholtz.

The numerical results reached by us differ, as a whole, considerably from those given by Mayer for interruptional beats in either of his papers, though the divergence is less than that between the two series representing his own observations and those of Mrs. Seiler. In some cases, however, the agreement is very close. Thus, for Ut_2 we find the last trace of beats to occur when these are 46 in number. The number as observed by Mayer is 26, and as observed by Mrs. Seiler 45. For Ut_3 our figure is 70, and Mrs. Seiler's is 70 also.

For the other notes the divergence is wide, except for Ut_5, for which our results agree quite well with those obtained by Mayer himself. These differences may be due to the different way in which the variations of intensity in the beats progress, to the presence of pitch variations in interference beats, to the fact that in our method the musical interval of the beating notes increases as the beats increase in number, to mere differences in the estimation of the observers, or to some other less evident causes.

We find that the ratios between the number of beats producing the greatest harshness at different pitches and the maximum number of beats discernible at those pitches are as follows (Table III.). The numbers given are obtained by dividing the former number by the latter.

TABLE III.

Ut_2	Ut_3	Sol_3	Ut_4	Sol_4	Ut_5	Mi_5
0.41	0.37	0.36	0.31	0.30	0.30	0.32

These figures, as a whole, agree very well with the ratio (four tenths) given by Mayer, although the absolute numbers whose ratios are taken are quite different from his. Our results also seem to indicate a clearly marked fall in this ratio as the pitch rises.

A few experiments were made using Professor Mayer's method, with some slight modifications, in order to observe the judgment of the same ear upon beats of different kinds. The tuning-fork employed was kept in vibration continuously by electricity, and the rotating disk was driven by an electro-motor, which secured great constancy of speed. We were seriously troubled by the sound made by the rotating disk, which produced a sort of siren effect as its openings passed before the aperture of the resonator. For Ut_3 the maximum number of intermittences perceived was 50 per second. For Ut_4 the number was about 106. These figures are liable to an error of perhaps two beats, or even a little more for the higher pitch. Mayer's figures are 47, 78, respectively, for his own observations on these notes, and 70, 130, for those of Mrs. Seiler. It is clear that there are very great differences in the sensitiveness of different ears for the perception of rapid beats.

In another series of experiments, interruptions were produced by a break-wheel placed in a telephonic circuit with a magneto-telephone at each end. The sound of a tuning-fork was transmitted through the line, and any desired number of interruptions could be produced by varying the rate of rotation of the wheel. Considerable annoyance was experienced at times from sounds which apparently arose from microphonic action at the break-wheel. These can probably be avoided in future experiments by causing the wheel to divert the current from the receiver periodically, instead of interrupting it. The limits at which the beats disappeared, with the notes experimented upon, were as follows: Ut_4 48, Mi_4 56, Sol_4 69. These figures are the means of a number of observations, and are apparently true within less than one beat per second. Comparing this kind of interruptional beat with those given by Mayer's method, the maximum number perceptible seems to be smaller for the former than for the latter. This is probably due in part to the greater loudness of the sounds observed in the latter case, but there is another marked difference which must exercise an important influence upon the phenomenon under consideration. With the beats produced by the break-wheel the sound begins and ends almost instantaneously, so that sharply marked intervals of sound and silence of equal duration succeed each other. One would naturally expect the telephonic beats to be the more distinct of the two, which is not the case. The subject is one which requires further study as to the influence of the relative duration of sound and silence in the telephonic method, and of the relative size of the apertures in Mayer's method.

In the matters which we have thus far discussed in the present paper, our results are fully in accordance with the theory of consonance proposed by Helmholtz. In some other particulars, however, we are led to conclude that this theory is incomplete, at least.

Some years ago, in a paper read at the Philadelphia meeting of the American Association for the Advancement of Science, and of which an abstract was published in the Proceedings of that Society for 1884 (page 113), one of us called attention to the bearing of certain phenomena of binaural audition upon Helmholtz's theory as follows: —

"In connection with his study on the effects of beats in causing dissonance, Helmholtz considers the condition of the vibrating portions of the inner ear as to resonance and damping. In his remarks on the subject, he assumes that no notes are capable of beating with each other unless they both affect the same vibrating element of the inner ear. This view of the matter gives a purely mechanical action in the ear as the explanation of the physiological phenomenon of beats.

"In addition to the experiments of Koenig, in which beats were obtained between notes of very great intervals, there are certain phenomena of binaural audition which appear to prove that this view is incorrect, and that rather than, or at least in addition to, this mechanical interference of vibrations in the ear, there is a more obscure operation within the sensorium itself. I refer to the fact that beats may occur when the exciting sounds operate upon different ears, and also apparently between the after-sensation and the succeeding sound of mistuned unisons. Whether this last phenomenon can be observed when the after-sensation results from an impression made upon the opposite ear to that which is impressed by the succeeding sound, I do not know; but in view of the fact that two simultaneous sounds acting upon different ears may beat, I do not see why this result should not be possible.

"Now if beats arise between the after-sensation and a following sound, Helmholtz's view can be true only upon the supposition that the vibrating parts of the inner ear continue in motion as long as the after-sensation persists; and that there is no residual sensation capable of giving beats other than that which persists only as long as the actual vibration in the ear itself continues. Such a supposition seems quite improbable. Moreover, the phenomenon of beats in the case of sounds acting simultaneously upon different ears cannot be explained even upon this supposition. There must be some kind of *vibration*, using this term in the most general sense, or some kind of alternation of phase or state within the sensorium itself.

"There is no question as to the fact of the production of beats under the circumstances last mentioned. I have not only verified the fact by experiments conducted in the usual manner, but have also studied the beats produced when a tuning-fork is held close to one ear and the sound of a second fork, not quite in unison with it, is transmitted by telephone to the other, taking suitable precautions that the ear against which the receiving telephone was held was not affected by the sound of the neighboring fork. Beats were readily obtained, which grew weaker as the fork was moved away from the open ear and approached to the ear which was closed by the receiver. The same result occurred when, instead of mistuned unisons, harmonic forks were used, which gave beats with the fundamental."

In the experiments just cited, the fact that the fork gave feebler beats as it was moved towards the ear to which the telephone was applied seemed clearly to indicate that the beats were not likely to be due to sounds transmitted through the head from one ear to the other, or to the passage of the vibrations through the skull from the outer air. These experiments did not differ in other respects from those of previous observers. The beating of the sound persisting in one ear after excitation had ceased with a second sound falling upon the other ear was, in fact, observed by S. P. Thompson, in 1881.

The existence of such binaural beats as are under consideration was noted as early as 1874 by Mach, who assumed that the sound was conducted from one ear to the other through the bones of the head. S. P. Thompson has studied the subject very carefully;* and while he is evidently strongly inclined to believe that the phenomena are due to an interference of sensations not produced by the same ear, nevertheless he does not appear to consider this as a fact finally settled beyond all question, although to us his results seem to leave small room for doubt on the matter.

The important bearing of the existence of binaural beats upon some parts of Helmholtz's theory of audition does not seem to have been very fully recognized. This may be because of some question as to whether each sound did not after all really act upon both ears, even when apparently applied to one alone. From the nature of the case, it is very difficult to prove finally that there is no possibility of such conduction of sound from one ear to the other, but we have sought to study the phenomena of binaural beats under circumstances which render such conduction improbable in the highest degree. With this end in view, we have repeated most of the experiments of Thompson, and made such additional tests as suggested themselves to us.

The sounds of two tuning-forks placed in a distant room were conveyed to the ears telephonically over two separate circuits. These forks were struck by hammers actuated by electro-magnets placed in circuits separate from those containing the telephones, and governed by keys operated by the foot of the observer at the receiving end of the line. This method was found to be preferable to running the forks continuously by electro-magnetic means, as the currents used in the latter method were liable to act directly upon the transmitting telephone and cause disturbing noises. Very powerful magneto-telephones were used as transmitters and receivers. Mi_4 forks were used throughout the experiments, unless otherwise stated, on account of the remarkable intensity with which their tones were transmitted, this being approximately the natural tone of the diaphragm. The singular phenomena of the localization in the back of the head of the sensation caused by two notes in opposite phases when heard by separate ears, and the apparent wandering of the sensation from one ear to the other in the case of binaural beats referred to by Thompson, were always clearly recognized.

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* Philosophical Magazine, Vol. IV. p. 274; Vol. VI. p. 383, Vol. XII. p. 351; Vol. XIII. p. 406.

The method of experimentation precludes any fusion of the two sounds, except within the head; but to decide whether the beats arise from an interference of the sensations or from a mechanical interference in Corti's organ, we must investigate further. We tried to throw some light on this point by the following experiments. It is well known that the vibrations of a fork, even when of too small amplitude to be heard when held opposite the ear itself, can be made audible by pressing the stem of the fork against the bone of the skull, or, still better, against the teeth, the latter transmitting vibrations to the ears better than any other part of the head. A still more effectual means of making audible very small vibrations is to close the ear with a bit of beeswax and press the stem of the fork lightly against the wax. In this case the vibrations are transmitted to the membrana tympani by the small amount of air enclosed within the meatus, as is clear from the fact that the sound of the fork is heard on touching the wax long after it ceases to be audible on touching its stem to the pinna of the ear. Hence in this case there is no conduction to the middle or inner ear through the bones of the head. Whatever sound reaches the ear follows the ordinary path through the meatus to the membrana tympani. Now we found that the vibrations of a fork could be heard longer when touched to the wax in the ear than when held against the teeth. We therefore took two small tonometer forks making four beats per second, struck them very gently, and held their stems against the teeth; loud beats were heard in the ears just as they are ordinarily heard when powerful forks are sounded in the air. The forks were then held in this position until the beats had entirely ceased to be audible, when they were removed, and the stem of each was touched to the wax closing the two ears. Instantly the two notes were heard, faintly but distinctly, in the ears to which they were held, and accompanying them were faint beats seeming to wander in the head from ear to ear, as is always the case with binaural beats. In trying this experiment care was taken that no vibration should be imparted to the fork from a gentle blow given on touching its stem to the wax, and it was found that the liability of such an occurrence could be greatly diminished by covering the end of the stem with a layer of wax.

To make sure that these beats were not the result of imagination, we took forks giving four, eight, twelve, and sixteen beats per second at random, struck them lightly as before, but in this case held only one of them against the teeth, so as not to know the number of beats which ought to be produced. When this fork had ceased to be heard, we touched both forks to the wax in the ears, as before, and in every case the correct number of beats was at once heard. The experiment was varied slightly as follows. One ear only was closed with wax; the other was immersed in a large basin of water. The experiment was then repeated as above, with the difference that one fork, instead of being touched to the ear, was touched to the marble basin, its vibrations being transmitted to the enclosed ear through the water. The same results were obtained as before. These experiments were all carried on at night, when there was not the slightest disturbing vibration in the air. Together with another experiment described below, they lead us to conclude that aerial vibrations acting upon the ear are not transmitted through the skull or bony parts of the head from one ear to the other. The experiments cited certainly seem to bear out this view, at least for tones of feeble intensity. Furthermore, the fact that differential tones have not been produced binaurally leads us to believe that it is true generally, even for very intense sounds, that binaural beats do not result from sound conduction within the head.

In his experiments Thompson was never able to obtain differential tones unless the sounds were allowed to mingle before falling upon the ears. Our experiments fully bear out this result, which we have verified in the following ways: (1) By listening to Ut_4 and Mi_4 forks through the telephones. These notes were transmitted with more than sufficient intensity to give rise to a differential when heard in the ordinary manner; but with a telephone placed at each ear, not the faintest trace of such a tone could be heard. We also reached equally negative results on listening to Mi_4 with a telephone, and holding an Ut_4, Sol_4, or Sol_3 fork close to the other ear, or on leading their vibrations to the ear through a long rubber tube. (2) By Thompson's method of carrying the tones to the ears by means of rubber tubes (in our experiments about thirty feet long), the forks being struck, one in another room and the other outside of the window, to prevent their tones from mixing before reaching the ears. No differential tone could be heard. We also tried to use Koenig's forks for illustrating beat-notes, but their very rapid vibrations were so deadened by the tubing that they could only be heard very faintly. (3) By the same process as above, with the exception that the ends of the rubber tube were connected with cylindrical resonators which were blown as already described. This gave almost deafening tones in each ear, but not the slightest trace of a differential. But in this case, as also in (2), if the two tubes were connected to two branches of a Y tube, and a third rubber tube leading to the ear was connected to the third branch, the differential tone came out at once. (4) The most striking proof was the following. The ears being closed with wax, a brass rod about five feet long was held lightly against the wax in each. When the stems of forks struck by two assistants were pressed against the farther end of the rods, very loud tones were heard in the ears, unaccompanied by any differential tone. If, however, one of the rods was removed from the ear and pressed tightly against the head, or, better, against the teeth, a loud differential tone was heard at once in the ear against which the rod was placed. If both rods were held against the teeth or head, the differential tone was heard in both ears.

This apparent impossibility of producing differential tones when the primary tones are caused to actuate separate ears would seem conclusive of the point under discussion except for the fact that it might reasonably be argued that, if sound conduction through the skull occurred from one ear to the other, the vibrations thus conducted might act directly on the inner ear, and not indirectly through the membrana tympani and chain of bones, in which case no differential tones should arise, although beats could still take place in the manner assumed by Helmholtz. But our experiment with the brass rods, described above, shows that such tones are in fact readily produced when conduction to the ear takes place through the bones of the head. And if there were any material conduction of this kind, it certainly seems as if the very loud sounds used by us would have given evidence of it at least by the occasional production of differential tones when the sounds actuated separate ears.

The production of beats without the simultaneous action of the beating sounds upon the same ear seems, therefore, to be clearly shown from these facts: (1) Beats are produced by sounds falling upon the ears separately even when the greatest precautions are taken to prevent both from affecting the same ear. (2) Under no circumstances does it seem to be possible to produce differential tones by binaural combination, even when the separate tones are extremely loud. (3) In all cases in which the beating sounds have apparently acted separately upon the auditory apparatus of each ear, the singular phenomenon of encephalic localization of the beats has appeared, while this phenomenon has never been found present either when the two sounds acted simultaneously upon the same ear through the auditory canal, or when one of them was manifestly transmitted to the ear through the bones of the skull.

We are therefore led to the conclusion that the mechanism in which the interference causing beats takes place, and through the operations of which we consequently recognize the character of consonant and dissonant intervals, lies, in part at least, beyond the auditory apparatus of the inner ear. It seems to us clear that notes may beat when they do not affect the same vibrating elements of the inner ear, and that we must look to some more profound changes within the sensorium itself for a complete explanation of the phenomena under consideration.

It may be possible that there are two distinct causes of beating; one, that suggested by Helmholtz, which wholly or principally obtains when the two notes act simultaneously upon the same ear, and the other due to some different and more obscure action which obtains in the case of binaural beats. In this case quite different laws as to consonance might hold. The exceeding harshness of dissonances in binaural audition lends some support to this view.

Rogers Laboratory of Physics,
May, 1891.

II.

NOTE ON THE DEPENDENCE OF VISCOSITY ON PRESSURE AND TEMPERATURE.

By Carl Barus.

Presented January 13, 1892.

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1. *Historical.*— In the following paragraphs, I endeavor to give a preliminary account of what may be called the isothermals, the isopiestics, and the isometrics with respect to viscosity. Notwithstanding the great geological importance* of these relations, nobody has as yet attempted to represent them systematically.

2. *The Material chosen.*— In order to obtain pronounced results for the effect of pressure on viscosity, substances must be selected on which temperature has a similarly obvious effect. For, in addition to the direct access to the molecule which is beyond the reach of pressure, temperature has the same marked influence on the expansion mechanism per unit of volume increment as the other agency. Hence liquids like marine glue, pitch, etc., which change continuously from solid to liquid, and in which this change takes place at an enormously rapid rate and is complete within relatively few degrees, are especially available for the present investigation.

The following data refer to *marine glue.* Viscosity is considered as a physical quality, and apart from such chemical considerations as are introduced in passing from one body to another.

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* This will be indicated by Mr. Clarence King, for whom this work was done.

3. *Definitions.*—In my paper* on the absolute viscosity of the three states of aggregation, I defined a fluid (liquid or gas) as a body which, under constant conditions of pressure, temperature, and strain, shows constant viscosity as to time. In a solid, *cæteris paribus,* viscosity markedly increases with the time during which stress is brought to bear. The molecular instabilities of a liquid, therefore, are supplied at the same rate in which they are used in promoting viscous motion. In a solid they are used more rapidly than the small rate of continuous supply.

The point of essential concern in these definitions is the constancy of stress, and its value below a certain critical datum. For instance, if in a solid stress be *increased* at the (small) rate necessary to insure a constant supply of instabilities, then solid viscosity will also be constant, and I am by no means sure that in such a case † yield points would eventually present themselves as breaks in the continuity of the solid view.

On the other hand stress may be conceived to increase so fast, that even a liquid fails to present sufficient instabilities for truly viscous motion. The elasticity and brittleness of many viscous liquids, especially at low temperatures, is a case in point.

4. *Hardness.*—Throughout my work on viscosity,‡ I have adverted to the association of viscosity with zero forces acting for infinite times, and of hardness with infinite forces (relatively) acting for zero times, and have adduced many new examples showing the utter distinctiveness of these two properties. The subject of hardness has, however, recently taken more definite shape in the researches of Auerbach,§ based on a principle due to Hertz.‖ According to these observers, hardness is an expression for the elastic limits of a body in case of contact between its plane surface and the curved surface of some other (harder) body. Hardness so defined admits of absolute measurement in terms of dynes per square centimeter.

5. *Method of Work.*—In all experiments like the present, one cannot be too careful to preconsider the conditions under which the results are obtained; for one is only too apt to attribute an absence

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* Phil. Mag. (5), Vol. XXIX. p. 337, 1890. Cf. p. 354.

† Cf. Am. Journal (3), Vol. XXXIV. p. 19, 1887.

‡ Phil. Mag. (5), Vol. XXVI. p. 210, 1888. Cf. Bull. U. S. Geolog. Survey, No 73, pp. 42–44, 97, 98, 1891.

§ Auerbach, Wied. Ann., Vol. XLIII. p. 61, 1891.

‖ Hertz, Crelle's Journal, Vol. XCVI. p. 156, 1882.

of flow to the effect of pressure on viscosity, when the real cause is to be found in the geometry of the apparatus employed. I have therefore availed myself of transpiration methods, since the theory of the experiments is in this case very fully given.*

The marine glue, § 2, was forced out of a sufficiently large reservoir, through tubes of steel about 10 cm. long, and 0.5 to 1 cm. in diameter. Pressures as high as 2,000 atm. were applied at the reservoir, by aid of my screw compressor.† Temperatures between 10° and 30° were kept constant by a suitable water bath. Throughout the work the flow was so excessively slow (amounting to an advance of only a few millimeters per hour), that Poiseuille's law was at once applicable. The only considerable source of error in the work is the occurrence of more or less incidental slipping. However, inasmuch as the outflow of marine glue is capped by a rounded surface, it follows that the flow is most marked at the axis of the tube compatibly with the theory of the experiment.

6. *Volume Viscosity.*— At the end of stated intervals of time (usually hours), the small cylinders of marine glue which had exuded were cut off with a sharp knife, and weighed. Now it was curious to note that these cylinders, left to themselves for about a day, showed a gradual and marked deformation, such that the originally plane bottom or surface of section eventually expanded into a symmetrical projecting conoid, with an acute apex angle of less than 45°. I take this to be an example of volume viscosity. The restitution of volume is greatest in the axis of the cylinder where the flow is a maximum, and where the matter has been crowded into the smallest space. As a whole, the experiment is somewhat puzzling, for it points to the occurrence of a notable amount of slowly reacting elasticity even in this truly viscous solid. Indeed, as time went on, a re-entrant conoid, corresponding to the projecting cone just described, gradually dimpled the second of the two surfaces of section. What is here indicated, therefore, is probably a surface of flow.

7. *Viscosity and Pressure. Isotherms.* — Table I. gives a summary of my chief results. The table is one of double entry, and the data contained show the absolute viscosity (η) of marine glue at the stated temperatures and pressures, in terms of one billion

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* In addition to the well known work of Poiseuille, cf. Hagenbach, Pogg. Ann., Vol. CIX. p. 385, 1860; Osborne Reynolds, Phil. Trans., Vol. III., 1883, p. 935; Wilberforce, Phil. Mag. (5), Vol. XXXI. p. 407, 1891.

† These Proceedings, Vol. XXV. p. 93, 1890.

g/cs units. The pressure excess is the difference of pressures at the two ends of the tube.

TABLE I. — MEAN VALUES OF $\eta/10^9$ FOR MARINE GLUE.

Δp = Pressure Excess =	100 atm.	300 atm.	1000 atm.	1500 atm.	2000 atm.
Temperature = 8.5°	—	—	> 30 000*	—	> 60 000*
" = 18.3°	(2.5)	—	8.30	12.0	15.2
" = 22.5°	—	—	1.12	—	2.2
" = 30.5°	.065	.073	—	—	—
Rates at	8.5°	18.3°	22.5°	30.5°	
$10^{-9} \times \Delta\eta / \frac{1}{2}\Delta p =$	—	.0137	.00220		
$\alpha = \Delta\eta/\eta_0 \times \frac{1}{2}\Delta p =$	—	.0091	.020		

In constructing the rate of change of viscosity with pressure, I assumed that the whole thread *transpired at the mean pressure at the two ends of the steel tube*; or since the pressure at the open end is zero, at half the pressure excess. Furthermore, that

$$\eta_p = \eta_0 (1 + \alpha p) = \eta_0 (1 + \tfrac{1}{2} \alpha \Delta p).$$

If therefore $\Delta \eta$ be the increment of viscosity corresponding to the pressure $\frac{1}{2} \Delta p$, the final data of Table I. (rates) are at once intelligible.

In view of the occurrence of the arbitrary variable η_0, it is hardly probable that α would be independent of temperature. If reference were made to some other pressure, viz. $\alpha' = (\eta_p - \eta_0) / \eta_P$, the values of α' approach each other in proportion as P is larger. Thus, for $P = 1000$ atm., $\alpha' = .009$ at 18°.3 and $\alpha' = .010$ at 22°.5. The point of immediate importance here, however, is that *in proportion as the viscosity of a body increases with fall of temperature, its isothermal rate of increase with pressure also increases*; and that the rate of increase in the latter instance is a coefficient as remarkably large as $\alpha = .01$ to $.02$.

8. *Viscosity and Temperature. Isopiestics.*—Table I. also enables me to construct the approximate isopiestics for $\Delta p = 0$, 500,

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* No flow perceptible after five hours, in case of a tube 10 cm. long and 1 cm. in diameter.

1000, and 2000 atm. These loci are distinctly curved, showing that viscosity decreases at an accelerated rate with rise of temperature.

9. *Conditions of Constant Viscosity. Isometrics.*—In order, however, to compare the relative effects of temperature and pressure, it is necessary to map out the lines of equal viscosity for marine glue. I endeavored to do this by constructing Table I. graphically; thus I attained the data of Table II., where Δp is the pressure excess corresponding to the temperature θ, for the case in which the viscosity η has the value given at the head of the table.

TABLE II. — ISOMETRICS AS REGARDS VISCOSITY FOR MARINE GLUE.

$\eta = 1 \times 10^9$		$\eta = 2 \times 10^9$		$\eta = 3 \times 10^9$		$\eta = 5 \times 10^9$	
Δp	θ	Δp	θ	Δp	θ	Δp	θ
atm.	° C.	atm.	° C.	atm.	° C.	atm.	° C.
0	19.1	0	17.7	0	16.8	0	—
500	21.7	500	20.4	500	19.6	500	18.3
1000	22.8	1000	21.4	1000	20.6	1000	19.4
2000	24.3	2000	22.7	2000	21.8	2000	20.5
$\beta = .0030$		$\beta = .0026$		$\beta = .0024$		$\beta = .0022$	

There are thus given a family of lines of decreasing curvature. Supposing them to be eventually more nearly linear I have constructed $\beta = \Delta\,\theta / \frac{1}{2}\,\Delta\,p$ (where $\Delta\,\theta$ and $\frac{1}{2}\,\Delta\,p$ are the corresponding increments of temperature and pressure for constant viscosity) for the region between $\Delta\,p = 1000$ and 2000 atm. See Table II. These values, crude as they are, have an important geological bearing on the fluidity of magmas. I infer that in a field of high pressure as small a rise of temperature as 1° C. will quite wipe out the increment of viscosity due to a pressure as large as 400 atmospheres.

10. *Isothermal Flow through Tubes.*—Let there be given a tube of length l and radius ρ. Let $\eta = \eta_0\,(1 + a\,p)$ be the viscosity of the viscous liquid forced through it by the pressure excess $\Delta\,p = 2\,p$ (so that there is no pressure at one end of the tube) and at the constant temperature θ. The length λ of the cylinder of fluid issuing per unit of time (t) will be

$$\frac{\lambda}{t} = \frac{\Delta p \rho^2}{8 l \eta_0 (1 + \frac{1}{2} a \Delta p)}.$$

Hence the maximum flow will occur when $\Delta p = -2/a$, or, as negative pressures are excluded, the function λ/t is of a kind continually increasing with Δp.

11. *Measurement of excessively high Pressures.*—In view of this property of λ/t, it is worth inquiring in how far the transpiration method is available for high pressure measurement, when all other means fail.

Take for example marine glue, and a tube $\frac{1}{16}$ inch in diameter and 1 inch long. Then the mass m of marine glue which at 18°.3 would exude per hour is given in Table III.

TABLE III.—TRANSPIRATION OF MARINE GLUE, PER HOUR, AT 18°.3 C.

$l = 2.5$ cm. $\rho = .08$ cm. $\eta = 1.5 (1 + .009\frac{1}{2} \Delta p) \times 10^9$.

Δp	=	1000,	5000,	10000,	15000,	20000	atm.
$m \times 10^6$	=	4232,	4949,	5060,	5096,	5115	grams.

Thus it appears that whereas a hole $\frac{1}{16}$ inch in diameter may be efficiently sealed by marine glue at 18°.3 C., pressure measurement by aid of the exuding mass is impossible above 10,000 atm., whereas even between 5,000 atm. and 10,000 atm. the method is insensitive. To use a method like the present for very high pressure measurement, a substance of smaller pressure coefficient must therefore be sought, if such a one with other necessary qualities, exists. It is with the object of searching for such a body, as well as of finding the maximum of hydrostatic pressure attainable in the laboratory, that I had a tinned screw and socket constructed,* and hope to be able to report the results of my work at an early opportunity.

PHYSICAL LABORATORY U. S. GEOLOGICAL SURVEY.

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* These Proceedings, Vol. XXV. pp. 94, 108, 1890.

III.

WHAT ELECTRICITY IS: ILLUSTRATED BY SOME NEW EXPERIMENTS.

By W. W. Jacques.

Presented January 13, 1892.

Electricity is, to all of us, more or less surrounded with an atmosphere of mystery.

When we speak of Light, or Sound, or Heat, we feel that we are dealing with familiar things, — things so familiar to our every-day life that it seems useless to try to define or describe them. Every day the sunlight fills all space; it dazzles our eyes; it falls upon the objects around us, and makes them visible; and though through the evening, when the sun is gone, we substitute for a while a gas flame, or a candle, or an electric light, we have then through the day had so much of it that at night we are glad to be rid of it, and have darkness for our hours of repose.

So, too, from babyhood to old age, all day long and every day, we are listening to one or another sound, whether the voices of friends, or the busy hum of city life, or the delights of music, or the ticking of the clock at night. Indeed, so constantly are our ears filled with sounds, that, when we go alone on to a high mountain, or a desert plain, where there are no trees to rustle with the wind, the silence is painful and oppressive and awful.

Heat, too, is equally familiar, perhaps even more so: for what is more familiar than the warmth of sunshine? And is not the fireside the very centre, as well as emblem, of our home?

When, however, we speak of that other great force of nature, *Electricity*, we feel that we are departing from familiar ground. It is shrouded in mystery; it is something we cannot see, or hear, or feel, — something we cannot easily describe or define. We speak of it in the same breath with spirits and with ghosts. The reason, I take it, is because the human body has no organ especially adapted to recognize electrical phenomena. While the eye receives the ray of light, the ear the ray of sound, and any part of the surface of the body feels the heat, the presence of electricity cannot be detected by any of our senses. Electricity cannot be seen, or heard, or felt; it is tasteless and odorless.

Subjectively considered, then, electricity eludes our grasp.

Objectively, however, electricity is as familiar to us as light, or sound, or heat. Its phenomena have been as carefully studied, and its laws are as accurately known.

Let us for a moment recall the physical explanation of light and sound. Let us picture to the eye of the imagination the mechanics of a ray of light.

When we stand out of doors on a cloudless night and look above us, we see a multitude of stars. The telescope tells us that some of these are suns, some are moons, and some are other worlds than ours.

The nearest of them is distant millions of miles, and yet we can see them. There is a chain of something linking the star at which we are gazing to the eye. This chain we call, familiarly, a ray of light. Physicists tell us that along the pathway from the star to our eyes there are chasing each other with enormous speed a multitude of waves of light.

If we turn our eyes to another star, it too sends to our eyes its waves of light. If we go to a distant part of the earth, the same stars send rays of light to us there. And so we find that each of the multitude of stars is radiating ceaselessly in all directions multitudes of waves of light.

Between us and the stars, and between the stars extending everywhere through visible space, is the medium that transmits these waves, crossed and intercrossed continually with countless waves of light,— a medium rarer than the rarest gas,— the medium that is still left in space when we remove from it all solids and liquids and gases, *the ether*.

Objectively considered, then, light is a wave motion of the ether that everywhere surrounds us and fills all space. By a similar wave motion, but in a coarser medium, the air, sound is transmitted from place to place.

By means of his vocal organs, a public speaker moulds the current of air that issues from his lungs into waves of sound. These waves of sound are radiated in all directions, and fall upon the various listeners' ears.

Something analogous takes place when we drop a pebble on to the surface of a placid lake. From this centre of disturbance, waves of water are radiated in all directions until they reach the shore. Waves are likewise radiated downward to the bottom of the lake, and fishes have organs, like our ears, that enable them to take cognizance of these vibrations.

In the case of waves of water, or waves of sound, or waves of light, we know there is no bodily transference of a particle of water, or air, or ether, from the centre of disturbance to the shore, or ear, or eye. Each particle moves at the most only through a minute fraction of an inch; but each pushes the next, and this the next, so that motion, and not matter, is what is transmitted to a distance. Indeed, this propagation of motion, in contradistinction to propagation of matter, is the essential characteristic of wave motion.

Who has not seen a wave pass over a field of grain? Each particle bows its head but for a few inches, yet the wave passes on to the utmost limit of the field.

Sound, then, is a wave motion transmitted through the air. Light is a wave motion transmitted through the ether. But both of these media are also capable of having set up in them currents in which there is an actual bodily transference of the medium from place to place through considerable distance.

In the case of air, we call this motion the wind. In the case of the ether, I propose to show that it is a current of electricity.

As wind is the bodily forward motion of the medium whose vibratory motion we call sound, so a current of electricity is the bodily forward motion of the medium whose vibratory motion we call light.

A current of electricity is a breeze of light.

We may, perhaps, best get a realistic conception of electric currents, whether flowing through open space, or confined to a specially provided metallic conducting path, by first picturing to ourselves the phenomena of air currents, with which we are more familiar, and then mentally transferring these phenomena from the air to the more subtle medium, the ether. The analogies are very striking, and will materially aid the imagination in picturing electrical phenomena.

In the islands of the Pacific Ocean there is almost always a breeze, either from the land to the water, or from the water to the land. In the daytime the island is heated by the sun, its air is rarefied and rises, and the cooler breeze rushes in from the ocean to take its place. At night the island cools, the air descends, and an outward breeze is produced. There is always a breeze from an area where the air is condensed, and towards an area where it is rarefied. This local condensation and rarefaction of the air are the cause of breezes and winds and hurricanes. The maps issued by our weather bureau show areas of high and areas of low barometer, and the direction of the wind is always from the one to the other.

If, instead of allowing the wind to blow freely through space, we confine it to a narrow channel,— if, for instance, we produce an air pressure at one end of a long iron pipe, we get through the pipe a strong current of air, — as, for example, in pneumatic tubes, in which the current of air carries along small carriages, in the tin pipes used to convey the hot-air currents from our furnaces to the registers, and in the pipes used for distributing illuminating gas from the central gasometer to the houses about the city where it is burned.

The wind blowing through space is made evident to our eyes by its scattering of a handful of dry leaves, or dust, or bits of paper. It bows and bends the branches of the trees. A candle flame exposed to it is distorted, or instantly blown out. Its direction is more accurately indicated by the familiar weather-vane, and its strength is measured, if we will, by the anemometer.

As with the wind of nature, so too with the electric wind. If we substitute for our Pacific island a metal ball suspended in mid-air by a silken cord, and let the ocean be represented by the surrounding atmosphere on a moist day, and produce upon the ball an area of *electric* condensation, or, as an electrician would say, a positive electric change, we shall have an electric breeze blowing outward in all directions, which will last so long as the electrification of the ball is above that of the surrounding air. This may be made evident to the eye by placing upon the ball a handful of bits of paper, or dry leaves, or dust, any of which will be instantly blown away and dissipated in all directions. If a lighted candle be brought near the ball, its flame will be bent by the breeze, and possibly be blown out.

If instead of allowing this electric wind to blow away in all directions we confine it to a narrow path,— if, for instance, we connect the ball to the earth by a metallic wire, — we get through the wire a strong current of electricity, whose direction may be determined by the electric weather wave, a magnetic needle, and whose strength may be measured, not with the anemometer, but by the galvanometer.

We may conceive of this electric wind as a breeze of the ether: the proof of the identity will be given later.

It is in currents flowing along metallic wires that the phenomena of electricity have been most carefully studied, and it is the phenomena of such currents that have therefore been for the most part utilized in electrical inventions.

Nature's wind is used to waft our ships across the seas, and it is perhaps not a wild idea to conceive of electric repulsion utilized to support and propel heavily laden air ships through the space above our heads; but it is with electric phenomena as they have been investigated and utilized up to the present time that we have to deal in this article, and this, as we have seen, means the phenomena of electric currents flowing through metallic wires.

What are some of these phenomena?

Electricity — or what we shall soon see is the same thing, a current of ether — passes readily through a copper wire. To the ether current, the wire is hollow; in electrical terms, it is a good conductor. It also passes quite readily through an iron wire, but not so readily as through copper. It passes still less readily through a wire of carbon. It passes more readily through a large wire than through a small wire. In all wires, there is more or less ethereal friction or electric resistance.

In virtue of this ethereal friction or electric resistance, the current heats the wire through which it passes,—of course heating a small wire more than a large one, and heating an iron wire more than one of copper, and a carbon wire most of all. We see this in our household system of electric lighting. The current passes from the central station and throughout our houses to the lamps, over comparatively large wires of copper, which it warms only slightly; but coming to the lamps, it passes through a fine wire of carbon, in which the friction and consequent heating is so great that the filament becomes white hot; and were it not contained in a glass globe, from which the air has been removed, it would take fire and disappear.

Again, an electric current flowing in a wire coiled around a bar of iron converts the bar of iron into a magnet, so that it may attract an iron armature placed near its end, and thus do mechanical work. The converse of this is equally true, and if we move an iron armature to or from the end of an iron bar around which a wire is coiled, an electric current will be set up in the same coil, and by means of the connecting wires may be carried to a distance and utilized. On this latter principle depends the dynamo machine, which furnishes electricity to be used for light or power. On the former depends the electric motor that propels our street cars, and furnishes power to many of our industries.

Again, the electric current flows through wires with enormous velocity, and consequently it offers an excellent vehicle for the rapid communication of intelligence, — for telegraphy. A telegraph wire between two cities is merely a path through which the current may readily flow. At one end is a reservoir of electricity. The "key" is a device by which electricity may be allowed to flow into the line. By allowing small quantities of electricity to flow into the line at intervals of time in accordance with a pre-arranged code, and noting at their distant end their arrival, we may communicate any ideas that are capable of being expressed in such a code.

The arrival of these little currents of ether may be manifested to the eye in various ways. In the so-called needle telegraph, the current passing by a magnetic needle causes it to point in a given direction, just as the wind passing a weather-vane causes it to point in a given direction.

If it were possible to have on one hill-top a reservoir of air under pressure, or wind, and a key by which small puffs of air could be let out at intervals in accordance with a pre-arranged code, and on a neighboring hill a weather-vane, we might thus have a wind telegraph operated exactly as is the electric telegraph. But such a telegraph would be slow and cumbersome in operation, and is not likely to come into general use.

There is one other phenomenon on which I desire to dwell a moment, — a phenomenon of great importance, as it furnishes the first proof of the identity of electricity and the ether.

Suppose we have an ordinary telegraph wire in which there is a steady current flowing. Suppose ten feet away from this wire, and entirely disconnected from it, we arrange a short wire with any suitable means of detecting an electric current in it, should such a current exist. So long as the current in the first wire flows steadily on, there will be no current in the secondary wire. If, however, the current in the first wire be broken up into rapid pulsations, say 100 per second, by rapidly opening and closing the circuit we shall find in the secondary wire short pulsating currents occurring with the same frequency. How does this action take place? How are the impulses transmitted across apparently unoccupied space? The only conductor between them is possibly the moist air; but the same phenomenon takes place if the air be dry, or even if it be entirely removed. The only remaining explanation is that the pulsations are carried from one wire to the other by means of the intervening ether which we know fills all space. We shall see in a moment that the pulsations are transmitted by means of a wave motion of the ether from the one wire to the other.

Meanwhile, let us look at the analogy of this phenomenon as it takes place in a current of air.

Suppose we have a pipe in which there is a steady current of air flowing. Suppose ten feet away we place our ear. So long as the current of air flows steadily on, no sound will be heard. If, however, the current in the pipe be broken up into rapid pulsations, say 100 per second, by rapidly opening and closing its end, which may be done by means of a reed such as is used in organs, the pipe will radiate in all directions waves of musical sound of a pitch due to 100 vibrations per second, and this sound will of course be heard by the ear. In this case we have a current of air, by rapid interruptions, converted into waves in the air, or sound.

Analogy indicates that, in the former case, we had a current of ether (or electricity), by rapid interruptions, converted into waves in the ether (or electrical waves). But we must have stronger proof than the indications of analogy, and it is readily forthcoming.

If the interrupted current in the wire radiates ether waves, these ether waves are really nothing more nor less than waves of light. Unfortunately, the eye only detects waves of light that are a small fraction of an inch in length, while the waves radiated from the most rapidly interrupted electric current are many inches in length. Nevertheless, the complete identity of waves radiated from an interrupted electric current and from a source of light has been confirmed by the study and identification of many of their phenomena, first by Maxwell, and later by Hertz; the most striking proof being that waves radiated from an electric wire are propagated through space with a velocity of 300,000,000 meters per second, which is the same as the velocity of light.

So far as wave motions are concerned, therefore, those radiated from an electric wire are just as much ether waves as those radiated from the sun, or any other source of light.

It remains now to show the identity of the electric current and a current of ether. For this I invite your attention to some experiments of my own, that seem to me to go far towards establishing this identity.

If we can find somewhere in nature a breeze of ether blowing with the necessarily enormous velocity freely through space, and show that it exhibits both qualitatively and quantitatively the same properties as an electric current, the simplest possible supposition that we can make is that they are identical.

Now, the earth in its daily journey round the sun rushes through the ether that fills all space with enormous velocity, and to the observer on the surface of the earth this is the same thing as if the earth were at rest and the ether flowed by with this same velocity. Just as the observer on the deck of a swift steamship at sea feels the same breeze, whether the ship moves forward with a speed of twenty miles an hour through a calm atmosphere, or the breeze blows with a velocity of twenty miles an hour by the steamship when at anchor.

Now, our problem is to detect and measure this ether breeze, and show that qualitatively and quantitatively it possesses the properties of a current of electricity. This I have done in the following way.

Before us stands a very sensitive balance, capable of detecting a variation in weight of one part in a million. I have replaced the scale-pans with thin disks of brass, ten centimeters in diameter. Above and below each disk, and supported from the floor of the balance by glass legs, are other similar disks of brass. The two suspended disks are, of course, free to move up and down, but remain at rest so long as the equilibrium of the balance is undisturbed.

The remaining four disks are rigidly fixed, excepting as each can be raised or lowered by a delicate micrometer screw. For convenience I will designate the right-hand disks *Rt, Rm,* and *Rb,* indicating respectively right-hand top, right-hand middle, and right-hand bottom. Similarly, I will designate the left-hand disks *Lt, Lm,* and *Lb.* By means of a suitable battery I may electrify any of these plates, either positively or negatively.

Suppose, now, I electrify the beam of the balance, and consequently plates *Rm* and *Lm* positively. If the distances between plates are in all cases the same, the index will remain at rest. If it deflects, we know the distances are somewhere unequal, and must be adjusted by means of the micrometer, until there is no deflection.

If, now, I electrify Rt negatively, it will attract and lift Rm, and the index will move to the right.

If, however, I at the same time electrify Lb positively, it will tend to repel and lift Lm, and, as the repulsive lifting of Lm is equal to the attractive lifting of Rm, the index will remain at rest. That is, an *attraction* between Rt and Rm is balanced by a *repulsion* between Lb and Lm.

If, now, I suddenly change the electrification of the beam of the balance, and consequently of the plates Rm and Lm, to negative, we have a *repulsion* between Rt and Rm, balanced by an *attraction* between Lb and Lm.

Now, it can be shown by purely mathematical reasoning from electric phenomena, (see Maxwell's Electricity and Magnetism, Chap. XIX.,) that an ether current flowing between two positively electrified plates would, provided it possessed the electro-magnetic properties of a current of electricity, diminish their repulsion. If it flowed with the velocity of light, and had quantitatively, as well as qualitatively, the electro-magnetic properties of a current of electricity, it would just *neutralize* the repulsion.

If, on the other hand, it passed between two plates, one of which was charged positively and the other negatively, it would just double their attraction.

If, instead of moving with the velocity of light, 300,000,000 meters per second, it moved only $\frac{1}{10000}$ as fast, or 30,000 meters per second, the repulsion between similarly electrified plates would be diminished by one part in ten thousand, and the attraction between oppositely electrified plates increased one part in ten thousand.

Now, it can be further shown from purely astronomical measurements that our balance is, on the 22d of December at noon, carried through space with a velocity of 30,000 meters per second.

Observations made at noon on that day, then, ought to show the index of the balance one side of the position of equilibrium when the movable plates are electrified positively, and the other side when electrified negatively. The difference should indicate a total change of force of one part in twenty-five hundred.

This deflection of $\frac{1}{2500}$ is that due simply to the rotation of the earth around the sun. That due to the rotation of the earth about its axis is too small to note. But the whole solar system is moving towards Hercules with a velocity of 8,000 meters per second.

On the 22d of March this velocity would have to be added to the velocity of the earth in its orbit, and on the 21st of September subtracted. On the 22d of December it would have no effect. Our deflection on March 22d, then, should be about $\frac{1}{2000}$; on December 22d, $\frac{1}{2500}$; and on September 21st, $\frac{1}{2700}$.

Of course, in actually taking observations, it is necessary to use all six of the plates variously grouped and variously electrified, in order to get rid of accidental phenomena.

Even then the accidental phenomena frequently mask that for which we are searching, and it is only from the discussion of a considerable series of observations that results of value are obtained.

I began my observations last September, and have continued them at intervals since. The results observed are of the order of magnitude predicted, and vary, as expected, with the season of the year.

If, continued until next September, the cycle is complete, I shall feel even more sure of having discovered the phenomenon for which I am searching, and of showing that the motion of the ether possesses, both qualitatively and quantitatively, the properties of an electric current, — that *an electric current is a bodily forward motion of that same ether whose undulations we call light.*

IV.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY.

XVII. — FURTHER ADDITIONS TO THE NORTH AMERICAN SPECIES OF LABOULBENIACEÆ.

By Roland Thaxter.

Presented by W. G. Farlow, March 9, 1892.

The present paper includes the additions which have been made during the season of 1891 to the previously recorded species of North American Laboulbeniaceæ, a small number only of new forms being reserved for later description from lack of sufficient material. Three new genera are represented, — Ceratomyces by two species, Corethromyces and Acanthomyces each by a single species. The genus Heimatomyces, formerly including a single European form, contributes ten species, nine of them new while, lastly, the genus Laboulbenia adds sixteen species, thirteen of which are undescribed. In all thirty species, by which the sum total of American forms is increased to forty-nine. The material examined was collected by the writer partly in Maine, partly in Connecticut; while very important additions have also been received through the kindness of correspondents, from whom the communication of hosts likely to be infested has been solicited. For such courtesy the writer is especially indebted to Mr. Theo. Pergande, who has sent Coleoptera collected in the vicinity of Washington, D. C., and to Miss A. M. Parker, for numerous interesting specimens taken at Slaughter, Washington. Mr. J. M. Aldrich has also kindly sent specimens from South Dakota, and Mr. Samuel Henshaw has determined the greater part of the insect hosts. For all these favors, the writer desires to express his grateful acknowledgments.

The contribution of aquatic forms is of especial interest, the genus Ceratomyces forming a distinct departure from previously described generic types. The considerable addition, also, to the species of Heimatomyces serves accurately to define the characters of this genus, which proves to have been based by Peyritsch almost wholly on specific characters; while it is more than probable that the same author's genus Chitonomyces is also similarly based, and should be united with Heimatomyces. No specimens of the former genus being accessible, and the published figures leaving much uncertainty as to its true nature, the name Heimatomyces has been chosen to distinguish the American forms, their generic identity with *H. paradoxus* being unquestionable. The type of the genus is a very simple one, and may be characterized as follows.

HEIMATOMYCES, Peyritsch.

Receptacle consisting of a basal and terminal portion: the basal including five cells, the two lower superposed, the three upper small and forming the base of the perithecium: the terminal portion including four cells more or less connected laterally with the perithecium, the terminal cell always free, bearing at its rounded apex a single simple thread-like appendage: the subterminal cell free from or connected on its inner side with the two remaining cells, the upper of which gives rise, from the angle made by the inner wall of the perithecium, to several simple thread-like evanescent appendages (trichogyne and antheridia?). Perithecium simple or appendiculate, symmetrical or asymmetrical. Asci sublenticular, 4-sporic, spores fusiform or subfusiform, septate.

In a single species (*H. Halipli*) the middle of the three cells which usually form the base of the perithecium is enlarged, and extends the whole width of the receptacle, the base of which thus consists of *three* superposed cells. The terminal and subterminal cells of the receptacle may be elongated or modified; but the total number and general relative position of the cells seem to be very constant. In only two species, *H. paradoxus* and *H. appendiculatus*, is the perithecium modified by an outgrowth from one of its cells.

HEIMATOMYCES SIMPLEX, nov. sp.

Pale yellowish or faintly brownish. Perithecium rather slender, continuing the strong curve of the receptacle evenly outward to its rather coarse blunt apex. Basal cell of the receptacle much longer than the flattened sub-basal cell, the septum between the two often obsolete: terminal cell bell-shaped, small. Spores 26 × 11 μ.

Perithecia 55–60 × 11–12 μ. Length of receptacle 75 μ. Basal cell 15 × 7.5 μ. Total length 90–100 μ.

On *Laccophilus maculosus, Hydroporus spurius*, etc., Connecticut.

A very common species, occurring in considerable numbers on the elytra of the host, possessing the simple typical structure of the genus, and distinguished by its evenly curved habit, blunt perithecium, and uniform color.

HEIMATOMYCES HYALINUS, nov. sp.

Hyaline or very faintly tinged with yellowish brown. Perithecium large, at first hunched externally, and bent inward near the apex, becoming nearly straight, tapering to the rather small apex, which is bent somewhat abruptly outwards at maturity. Basal and sub-basal cells of receptacle broad, nearly equal, or the basal twice as long as the sub-basal, the two separated by a well defined septum. Spores 8 × 2.5 μ. Perithecia 75–90 × 20 μ. Total length to tip of perithecium 110–120 μ.

On *Laccophilus maculosus*, Connecticut.

Differing from the last in its larger size, and stouter straight perithecium, as well as in minor points. It occurs only on the posterior legs of its host.

HEIMATOMYCES AFFINIS, nov. sp.

Rather strongly suffused with yellowish brown. Perithecia commonly slightly curved inwards, or nearly straight, the tips often slightly bent outwards. Basal cell of receptacle large, sub-triangular, suffused laterally and terminally with deep black-brown: sub-basal cell very flat; terminal cell small, its axis bent strongly inwards. Spores 50–55 × 3 μ. Perithecia 100–110 × 30 μ. Basal and sub-basal cells of receptacle 40–45 μ. Total length to tip of perithecium 150–170 μ.

On *Laccophilus maculosus* and *Hydroporus* sp., Connecticut.

Nearly allied to *H. hyalinus*, from which it may be separated by its larger size and suffused basal cell. It occurs at the apex of the right elytron.

HEIMATOMYCES APPENDICULATUS, nov. sp.

Becoming faintly brownish. Perithecium tapering to a rather sharp apex, curved strongly outwards, hunched externally (often distorted by twisting), and bearing a straight, sub-clavate, one-celled, brownish appendage arising externally below the apex.

Basal cell of the receptacle rather narrow, more than twice as long as the squarish sub-basal cell. Spores 32 × 3 μ. Perithecia 55 × 15 μ to 75 × 22 μ. Basal and sub-basal cells 30–45 μ in length. Perithecial appendage 30–33 × 4 μ. Total length to tip of perithecium 100–130 μ. Greatest breadth 30–36 μ.

On *Laccophilus maculosus*, Connecticut.

A rare species, confined to the anterior pair of legs of its host, and distinguished at once by its clavate perithecial appendage which corresponds to the similar horn-like projection from the perithecium of *H. paradoxus*.

Heimatomyces paradoxus, Peyr.

This species occurs not uncommonly on the edge of the left elytron of *Laccophilus maculosus* in company with *H. marginatus*. The ascogenic area is so placed that the asci and spores are much distorted at maturity; but the latter do not appear to have the peculiar shape represented by Peyritsch.

Heimatomyces Halipli, nov. sp.

Strongly suffused with yellowish brown. Perithecia inflated, more strongly externally, rounded to the papillate tip. Base of receptacle composed of *three* superposed cells, the lower triangular, suffused with blackish at the base; the two upper much flattened, their septa horizontal; terminal cell small; an inconspicuous truncate hyaline projection arising near the trichogyne. Spores 28–30 × 3 μ. Perithecia 100 × 35–40 μ. Basal cells 40–50 μ. Total length to tip of perithecium 150 μ.

On *Haliplus ruficollis* and *Cnemidotus muticus*, Connecticut.

Occurs rarely on the right elytron of its host, usually upon Haliplus, a single specimen only having been found on Cnemidotus. It is distinguished from all other species by the three superposed basal cells of the receptacle, the upper of which appears to be what is usually the middle of the three cells which normally form the base of the perithecium. The inflated, abruptly papillate perithecium is also a distinguishing character.

Heimatomyces lichanophorus, nov. sp.

Hyaline except for the suffused basal cell. Perithecia bent outwards at an angle from the basal part of the receptacle, tapering slightly to the papillate apex. Basal cell of receptacle enlarged and greatly elongated, more or less intensely blackened above its hyaline base; sub-basal cell flat and almost obsolete. Terminal and subterminal cells together forming a straight finger-like projection as long as or longer than the perithecium. Spores 33–37 × 2.5–3 μ. Perithecia 65–90 × 30 μ. Total length to tip of perithecium 150–180 μ. Basal cell 90–110 μ.

On *Laccophilus maculosus*, Connecticut.

This species is confined to the median inferior anal plate of its host, and has only been observed upon males. It is not to be confused with any other species, being distinguished by its elongated basal and apical cells, almost black and white color, and papillate divergent perithecium.

HEIMATOMYCES RHYNCHOSTOMA, nov. sp.

Evenly suffused with yellowish brown. Perithecia relatively large, abruptly hooked at the broad apex, so that the papillate tip is turned inwards and is lateral in position. Basal cell of receptacle comparatively short, slightly inflated: sub-basal cell flattened: terminal and subterminal cells forming an outwardly curved, finger-like appendage exceeding the perithecium; the subterminal cell continued into a short well marked hook. Spores 26 × 3 μ. Perithecia 75 × 22 μ. Total length to tip of perithecium 100 μ. Basal cells of receptacle 25–30 μ.

On *Laccophilus maculosus* and *Hydroporus spurius*, Connecticut.

Occurs rather rarely on the margin of the right elytron, from the surface of which the perithecium projects in a characteristic fashion. The broad hooked apex of the perithecium and the finger-like development of its distal portion distinguish this species from any other form.

HEIMATOMYCES UNCINATUS, nov. sp.

Evenly suffused with pale yellowish brown. Perithecia large, curving evenly inwards to the somewhat pointed apex. Basal cells of the receptacle rather slender, the terminal cell pushed to one side and bent past the apex of the perithecium by a somewhat indurated, blunt, hooked outgrowth from the subterminal cell. Perithecia 75–85 × 20 μ. Total length 110–130 μ. Basal cells of receptacle 37 μ.

On *Laccophilus maculosus* and *Hydroporus spurius*, Connecticut.

A rather rare species, occurring in groups on the inferior surface of the abdomen of its host, and distinguished by the peculiar development of the subterminal cell of the receptacle.

HEIMATOMYCES MARGINATUS, nov. sp.

Long and slender, at first nearly hyaline, then yellowish. Perithecia straight, then suddenly bent inward below the hyaline, neck-like, strongly curved tip. Basal cells of the receptacle subtriangular, the sub-basal half as large as the basal, the three cells at the base of the perithecium more than usually developed: the terminal cells all becoming black and opaque at maturity; the terminal one continued by a squarish outgrowth basally hyaline, at first lateral and external, becoming terminal (the true apex of the cell being pushed inwards and becoming lateral), hardly exceeding the tip of the perithecium which it conceals. Spores 30 × 3 μ. Perithecia 95–110 × 22 μ. Total length to tip of perithecium 140–160 μ. Basal cells of receptacle 25 μ.

On *Laccophilus maculosus* and *Hydroporus spurius*, Connecticut, Maine.

A form peculiar for the modification of the terminal cells of the receptacle, which makes the perithecium appear as if bordered by a black band. It is found in company with *H. paradoxus*, and recalls the supposed genus Chitonomyces, which is said to be similarly associated on the left elytron of its host.

CERATOMYCES, nov. gen.

Receptacle reduced, consisting of a small number of basal cells, above which it is directly continued by the basal cells of the perithecium and antheridial appendage. Perithecia highly developed, the walls composed of four longitudinal rows of superposed cells, the outer row continued into a horn-like appendage. Antheridial appendage arising at the base of the perithecium, composed of a series of superposed cells the upper angles of which may be cut off to form the base of filamentous appendages (antheridia ?). Asci subclavate, 4-spored. Spores fusiform or acicular, once septate, involved in mucus.

CERATOMYCES MIRABILIS, nov. sp.

More or less deeply suffused with yellowish brown. Perithecium elongate, the walls composed of longitudinal rows of superposed cells, about twenty-three in each row, the cells of adjacent rows alternating, their long axes transverse: the outer row continued below the apex of the perithecium as a curved horn-like projection, basally constricted and suffused, tapering distally to a rounded tip (in unbroken specimens), and made up of a series (ten to sixteen) of more or less cylindrical superposed cells. Tip of perithecium subhyaline, subacute, curved towards the perithecial appendage. Antheridial appendage arising from the receptacle slightly above the ascogenous cell of the perithecium; subconical, composed of a variable number of superposed cells, from the upper angles of which may be cut off, by an oblique partition, small cells which give rise to the antheridial branches, the latter slender, hyaline, septate, simple or branching, evanescent. Receptacle composed of three superposed cells, deeply blackened except along the outer edge, surmounted by a larger inner blackened cell and two smaller outer subhyaline cells; the basal cell partly subhyaline, the foot large and wedge-shaped, the axis of the receptacle strongly bent between the basal and sub-basal cells. Spores slender, one or more times spuriously septate, fusiform or slightly rounded at the apex, 100–120 × 4 μ. Asci flattened, subclavate on a short curved pedicel. Perithecia 280–295 × 65–75 μ. Antheridial appendage one half to two thirds as long as the perithecium. Perithecial appendage 180–200 μ. Total length to tip of perithecium (maximum) 450 μ. Receptacle 150 × 75 μ.

On *Tropisternus glaber* and *T. nimbatus*, Connecticut.

Taken in a single locality, at Milford. The trichogyne arises apparently from the angle between the perithecium and the antheridial appendage, thus indicating a probable relationship to the Heimatomyces section of the family. The parasite inhabits the inferior surface of its host in various positions.

Ceratomyces camptosporus, nov. sp.

Closely resembling the last in general appearance. Perithecia strongly curved near the base, proportionately stouter and shorter, each row of cells made up of from thirty-five to forty members, which, especially in the external row, are successively inflated, giving the outline on this side a strongly corrugated appearance: perithecial appendage of fewer, longer cells, not bent or blackened towards its base. Receptacle very small, triangular, straight, of not more than two or three superposed cells, the lower quite opaque. Antheridial appendage arising from a short curved basal cell, above which it is abruptly inflated, tapering thence to a rather slender apex. Spores more slender than in *C. mirabilis*, tapering at both extremities, slightly swollen and strongly bent near the base, 110 × 3.5 μ. Perithecia 275 × 85–90 μ. Receptacle 90 × 50 μ.

On *Tropisternus glaber*, Connecticut.

This species occurs with the last, but more rarely, and was at first mistaken for a mere variety of it. The differences, however, are important and constant, the peculiarity of structure presented by the spores being unique in the group.

CORETHROMYCES, nov. gen.

Receptacle reduced to a basal with two or three terminal cells, giving rise on one side to the free perithecium, on the other to several long straight rigid cylindrical jointed appendages, which bear externally at short intervals numerous secondary appendages.

CORETHROMYCES CRYPTOBII, nov. sp.

Perithecium (immature) long and narrow, the tip bent slightly inwards. Primary appendages three or four in number, brownish, rather closely 11–12-septate, cylindrical, straight, tapering slightly; the secondary branches simple, aseptate or pseudoseptate, somewhat divergent, comprising a row of larger brown appendages on either side, between which arise a few smaller hyaline ones; the larger appendages about equal in number to the segments of the primary appendage (six to seven). Receptacle opaque above the small hyaline basal cell. Primary appendages 150–160 × 8–10 μ; secondary appendages (longer) 100–110 × 5.6 μ. Receptacle 75 × 40 μ. Perithecium (immature) 100–110 × 20 μ.

On *Cryptobium pallipes*, Virginia (Pergande).

A single immature specimen of this remarkable genus was found growing on one of the posterior legs of its host. The highly differentiated appendages are quite different in character from those of any other genus. In their natural position they almost wholly obscure the perithecium, and, springing from the greatly reduced receptacle, present the appearance of a brush-like tuft, the true nature of which is not at once apparent.

ACANTHOMYCES, nov. gen.

Perithecia as in Laboulbenia, clearly differentiated from the receptacle. Main axis of the receptacle composed of superposed squarish cells, and, above its basal cell on the inner side, of a series of smaller appendage-bearing cells extending up to and around the base of the perithecium: the appendages simple, rigid, septate. Spores as in Laboulbenia.

ACANTHOMYCES LASIOPHORA, nov. sp.

More or less suffused with blackish brown. Perithecia borne on the apex of the receptacle, somewhat inflated, nearly symmetrical, tapering to a rather blunt apex. Appendages arranged in two rows of larger bristle-like members, hyaline at the tips, blackish below, running from the apex of the basal cell (one opposite each upper inner angle of the cells of the main axis) to the apex of the receptacle, where they envelop the base of the perithecium: from the cells of the receptacle between these two rows arise smaller appendages, which become more numerous towards its extremity. Receptacle slender at the base, expanding upwards, consisting of a main axis of about twelve superposed vertebra-like cells, at first hyaline, becoming blackish, and of a series of smaller cells almost completely concealed by the appendages. Spores involved in mucus, 1-septate, 30 × 3 μ. Perithecia 140–145 × 50 μ. Larger appendages 75–90 μ. Receptacle 175 μ.

On *Atranus pubescens*, Connecticut.

The slightly branched terminal trichogyne of this singular form is hidden between the appendages at maturity. The character of the antheridia could not be determined from the material examined, and the minute structure of the receptacle, apart from the main axis, is almost completely hidden by the appendages.

LABOULBENIA COMPACTA, nov. sp.

More or less tinged with olive-brown. Perithecia moderate, tapering towards the somewhat coarse-lipped, outwardly oblique apex. Pseudoparaphyses forming a dense tuft, hardly exceeding the perithecia in length, simple, or once branched above the basal cell, tapering evenly to the apex, 1–3-septate, tinged with brownish near the base: arising from a broad cellular base of eight or more cells, above a more or less well marked disk of insertion situated just above the base of the perithecium. Receptacle very short and stout, subtriangular: cell II. much broader than its length, wedge-shaped distally: cell III. greatly reduced, broad and flat: cell V. unusually large, its base resting on cell III. Spores 60 × 4 μ. Perithecia 110 × 40 μ. Pseudoparaphyses 90–100 μ. Total length to tip of perithecia 180–190 μ. Greatest breadth 65 μ.

On *Bembidium* sp., Maine.

A small well marked species of the *luxurians* type, differing in its peculiar shape and abundant straight appendages inserted on a multicellular base, which is more highly developed than in *L. luxurians* or *L. fumosa.*

LABOULBENIA LUXURIANS, PEYR.

A form which appears to be identical with this species, and closely allied to *L. fumalis,* occurs usually on the tips of the elytra of species of Bembidium in Maine, and has also been sent to me from Washington by Miss Parker.

LABOULBENIA VARIABILIS, nov. sp.

At first hyaline, becoming more or less tinged with brown. Perithecia moderate, tapering only slightly to the rather blunt, outwardly oblique, coarse-lipped apex, which is more or less deeply blackened below, especially on the inner side. Pseudoparaphyses very variable in number, sometimes hardly branched, sometimes forming a dense fascicle: arising more or less indefinitely from a small number of basal cells above cells IV. and V. of the receptacle, from which they are not separated by any disk of insertion: the basal portion short, constricted at the blackish septa, the segments slightly inflated; the distal portion slender, cylindrical, aseptate or obscurely septate, hardly tapering; often hardly exceeding the perithecium, sometimes several times its length. Antheridia overlapping one another on special lateral branches, forming a subconical cluster. The plane of insertion of the pseudoparaphyses usually opposite the middle of the perithecium, sometimes carried beyond its apex by the elongation of cells III. and IV. of the receptacle. Receptacle medium or much elongated; cell V. often enlarged, and protruded along the inner face of the perithecium, so as to throw the pseudoparaphyses and their insertion outwards. Spores 50–60 × 6 μ. Perithecia 92–130 × 33–50 μ. Pseudoparaphyses 150–480 μ. Total length to tip of perithecium 180–550 μ.

On *Omophron Americanum, Chlænius Pennsylvanicus,* Connecticut. On *Nebria pallipes, Chlænius æstivus,* Virginia (Pergande). On *Platynus extensicollis, Patrobus longicornis, Pterostichus corvinus,* S. Dakota (Aldrich).

A species remarkable for its great variation in size even on the same host, as well as the irregularities connected with the number and relative insertion of its pseudoparaphyses. The latter are peculiar from their differentiation into a basal short portion, composed of a small number of slightly inflated cells, and a distal filamentous, scarcely septate portion. The subconical clusters of antheridia are also quite peculiar to this species, and distinguish it from other known forms.

LABOULBENIA GALERITÆ, nov. sp.

Perithecia punctate becoming almost opaque, elongate, subcylindrical, slightly rounding to the base and rather abruptly tapering to the blunt apex: the latter slightly oblique outwards. Pseudoparaphyses simple, septate, slightly constricted at the lower septa and tapering towards the somewhat blunt apex: arising from a subconical, cellular base in (usually three) nearly vertical rows, from three to four pseudoparaphyses in each row: the base of insertion hyaline above, nearly black below, placed below the base of the perithecium. Receptacle moderate, or slightly elongate; cells III., IV., and V. externally, or almost wholly, opaque. The basal cells of the perithecium greatly enlarged and elongated, so as to form a distinct, stout, neck-like hyaline base, on which it is borne entirely free. Spores 50 × 5.5 μ. Perithecia 155 × 37 μ. Pseudoparaphyses (long) 350 μ. Total length to tip of perithecia 375 μ.

On *Galerita janus*, D. C. (Pergande).

This very distinct and peculiar species occurs, often in great numbers, on all parts of its host, and is distinguished by the insertion of its paraphyses on a subconical cellular base, as well as by the neck-like base of its perithecium.

LABOULBENIA GYRINIDARUM, nov. sp.

Blackish brown, nearly or quite opaque. Perithecia large, subconical or subcylindrical: usually straight externally, rounded internally; the apical lobes modified to more or less distinct, short, straight, simple appendages. Pseudoparaphyses hyaline or basally brownish, arising in a broad dense tuft from several basal cells, several times irregularly branched, rather closely septate basally and constricted at the septa, distally sparingly septate, slender, cylindrical; seldom extending more than two thirds of the distance from the base to the apex of the perithecium. Receptacle distally very broad, cells I. and II. short and slender, rarely elongate. Asci 4-spored, 150 × 37 × 18 μ. Spores 90 × 7–8 μ. Perithecia 190 × 90 μ. Pseudoparaphyses 100–110 μ. Total length to tip of perithecium 480 μ: greatest breadth 160 μ.

On *Gyrinus* sp., Connecticut.

This constitutes the second species of the genus which is peculiar to an aquatic host; but is quite distinct from the form represented by the excellent figures of Robin under the name of *L. Guerinii.* Its paraphyses recall those of *L. variabilis* in their general structure; but in no other species are they so densely tufted, while the appendiculate apex of the perithecium is unique in the genus. The species is a common one, growing upon the elytra as a rule, and was collected in numerous localities about New Haven.

LABOULBENIA BRACHINI, nov. sp.

More or less evenly suffused with amber-brown. Perithecia rather short and stout, tapering to the broad, often abruptly truncate, black apex, the lip edges of which are hyaline. Pseudoparaphyses hardly exceeding the mature perithecium, arising primarily from two basal cells, — a larger inner nearly hyaline, a smaller outer more or less opaque, — on which are closely set, so as to form almost a semicircle, the ten or more basal cells of the simple, slightly curved (outward) and tapering pseudoparaphyses, the inner hyaline, the outer blackened at the base. Disk of insertion oblique, in position between the lower thirds of the perithecium. Receptacle normal, short or sometimes elongate. Perithecia 125–185 × 75 μ. Pseudoparaphyses (long) 150 μ. Total length to tip of perithecium 550 μ (average 375 μ): greatest breadth 110 μ.

On *Brachinus* sp., Virginia (Pergande).

A species readily distinguished from *L. Rougetii,* which occurs in Europe on a similar host, by its fan-like pseudoparaphyses, amber color, and black-tipped perithecium. The specimens bearing the parasite, usually at the base of the elytra, were taken by Mr. Pergande in dry situations near Washington, D. C.

LABOULBENIA CURTIPES, nov. sp.

Olive-brown except for the hyaline contrasting basal cell of the receptacle. Perithecium large, containing very numerous asci and spores, inflated externally, nearly straight, the rather small apex strongly bent outwards. Pseudoparaphyses arising from two blackened basal cells, in a small tuft, slender, tapering, straight, inconspicuous, hardly exceeding the middle of the perithecium. Receptacle small and short in proportion to the perithecium; cell I. hyaline, contrasting with cell II., which is short, broad, and distally wedge-shaped. Spores 40 × 4 μ. Perithecia 110–135

× 55 μ. Pseudoparaphyses 55 μ. Total length to tip of perithecium 200–225 μ: greatest breadth 50–55 μ.

On *Bembidium bimaculatum*, Washington (Miss Parker).

This species occurs usually upon the posterior legs of its host, and is peculiar for the great number of spores which it produces in its unusually large inflated perithecia, the pseudoparaphyses being almost obsolete in mature specimens.

LABOULBENIA PARVULA, nov. sp.

More or less suffused with dark olive-brown. Perithecia slightly inflated, darker at the base and apex, the latter expanded slightly, rather large, the coarse lips oblique inwardly or nearly horizontal. Pseudoparaphyses exceeding the tip of the perithecium, arising primarily from two basal cells, above which from six to eight ultimate branches are formed, the outer larger, straight, divergent, nearly opaque at its base; the rest straight, nearly hyaline: disk of insertion black, just above the base of the perithecium in position, and producing a constriction at the apex of the receptacle. Receptacle short, cells III.–VII. becoming nearly opaque, cell II. less deeply colored, cell I. nearly hyaline, or suffused only on the outer side. Spores 35–40 × 4 μ. Perithecia 100 × 40 μ. Total length to tip of perithecium 165–180 μ: greatest width 44–50 μ.

On *Platynus extensicollis*, Virginia (Pergande). On *Bembidium bimaculatum*, Washington (Miss Parker).

A small species, without striking peculiarities, yet easily separated from any form known to me, and apparently constant in its characters, as shown by a comparison of material from two such widely separated localities as those above mentioned.

LABOULBENIA INFLATA, nov. sp.

Hyaline or slightly tinged with brownish. Perithecia rather small, straight, the tip bent outwards, a black patch below the rather coarse hyaline lips. Pseudoparaphyses two to four in number, peculiar from the inflation of the first two or three basal cells, above which they are rigid, thick-walled, curved slightly outwards, hyaline, tapering to a blunt apex; the basal cell of the outer pseudoparaphysis is much larger than the rest, short, flat, and much inflated. Receptacle normal, the cell walls unusually thick. Pseudoparaphyses 120 μ. Perithecia 85 × 30 μ. Total length to tip of perithecium 190 μ.

On *Bembidium* sp., S. Dakota (Aldrich).

The short inflated basal cells of the rigid, nearly hyaline paraphyses, associated with a definite disk of insertion, distinguish this small species from other forms with which it might possibly be confused. Three specimens only, in good condition, were found growing on the elytra of the host.

LABOULBENIA RECTA, nov. sp.

Olivaceous. Perithecia rather small, slightly rounded to the large, almost cylindrical, abruptly truncate, blackened apex, the lips of which may be very slightly oblique inwards. Pseudoparaphyses stout, arising from two basal cells, the outer twice as long as the inner, each giving rise to from two to three branches, which may in turn be once or twice branched, all the branches parallel to one another and to the main axis of the receptacle and of the perithecium, which they exceed by more than half its length: disk of insertion thick, black, horizontal, placed opposite the middle of the perithecium. Receptacle normal, rather elongate. Spores 75–80 × 6–7 μ. Pseudoparaphyses 175 μ. Perithecia 150–180 × 50–75 μ. Total length to tip of perithecium 380 μ: greatest breadth 75–110 μ.

On *Platynus extensicollis*, Connecticut.

A rare species, occurring on the legs of its host in company with *L. scelophila*, to which it bears some resemblance in the branching of its paraphyses. A small number of specimens from three localities near New Haven show little variation.

LABOULBENIA CONTORTA, nov. sp.

More or less suffused with reddish brown. Perithecia suffused with blackish brown, sometimes nearly opaque, considerably inflated, strongly curved outwardly at the apex, so that the nearly hyaline, very broad, hatchet-shaped lips are almost vertical in position: the whole perithecium at maturity usually so twisted near the base that its axis crosses the pseudoparaphyses obliquely. Pseudoparaphyses exceeding the perithecium by about twice its length, arising from two basal cells, the outer twice as large as the inner; the outer pseudoparaphysis simple or once branched above the subbasal cell, the inner sometimes branched above the basal and subbasal cells: disk of insertion thick, black, placed about one third of the distance from the base to the apex of the perithecium. Receptacle abruptly expanded above cell II., cells I. and II. rather elongate, the rest somewhat reduced and rounded. Spores 75 × 5 μ.

Perithecia 150–180 × 60–75 μ. Total length to tip of perithecium 330–400 μ: greatest width 90–100 μ. Pseudoparaphyses 300 μ.

On *Platynus extensicollis,* Connecticut.

This peculiar species occurs rarely on the inferior lateral face of the thorax of its host, seldom elsewhere, and is abundantly distinct from any other species of the *flagellata* type. The twisting of the perithecium is apparent only in mature specimens, yet this modification seems characteristic and analogous to the more pronounced distortion of the following species.

LABOULBENIA GIBBEROSA, nov. sp.

More or less faintly tinged with reddish brown. Perithecia short, stout, expanding slightly from the base to a conspicuous external hunch just below its broad, almost truncate apex. Pseudoparaphyses arising from a large outer and a very small inner basal cell, simple or bearing two to three branches always above the subbasal cell, constricted at the septa, the segments becoming slightly inflated, the tips usually curved and tapering: the disk of insertion small and thick. Receptacle elongate, strongly twisted above cell II., the twist continued by cells IV. and V., which are much elongated, and carry the pseudoparaphyses out at right angles to the axis of the perithecium. Spores 50 × 4.5 μ. Pseudoparaphyses 180 μ. Perithecia 125 × 50 μ. Total length to tip of perithecium 500–550 μ.

On *Platynus extensicollis,* Connecticut.

A number of specimens of this rare and singular species show that the twisted receptacle is a constant character, which is sometimes carried to such an extreme that the ordinary direction of the pseudoparaphyses is reversed, the elongation and curvature of cells IV. and V. bending them towards the base of the receptacle. The species is large and unusually elongate, growing on the inferior surface of its host, usually near the base of the middle pair of legs.

LABOULBENIA SCHIZOGENII, nov. sp.

Hyaline or pale yellowish. Perithecia rather short, smoky or nearly opaque, especially towards the apex, the prominent rounded hyaline lips of which are slightly oblique outwards. Pseudoparaphyses from two basal cells, each giving rise to two to four branches, which may in turn be one to three times branched: the branches all hyaline or pale yellowish, slightly curved and rounded at their extremities: disk of insertion small and thick, very oblique, placed above the middle third of the perithecium, from which it is wholly separated through the elongation of cell V. Receptacle usually elongate, cell V. being continued beyond the insertion of the pseudoparaphyses nearly to the lips of the perithecium, cells IV. and V. being thus almost superposed. Spores 70 × 5.5 μ. Perithecia 100–120 × 50–55 μ. Pseudoparaphyses (long) 270 μ. Total length to tip of perithecium 350–375 μ: greatest width 75 μ.

On *Schizogenius lineolatus* and *S. ferrugineus*, Connecticut.

A rare species, at once separable by the peculiar relative position of the pseudoparaphyses, and the unusual elongation of cell V., which is sometimes approached by specimens of *L. variabilis*.

LABOULBENIA PEDICELLATA, nov. sp.

Hyaline, becoming brownish, long and slender. Perithecia distally subconical, inflated on the inner side, the apex rather broad and usually somewhat pointed, nearly symmetrical. Pseudoparaphyses, when perfect, exceeding the perithecium, arising primarily from two basal cells, the outer twice as long as the inner, bearing at its apex a roundish cell, from which arise three branches two to three times subdichotomously branched, the branches curved and more or less hooked at the apex. After fertilization, the inner basal cell produces a number of branches curved towards the perithecium, and often producing secondary branches: disk of insertion rather broad, blackish, oblique, inserted just above the base of the perithecium. Receptacle long and slender through the great elongation of cell II. Spores 50 × 3.5 μ. Perithecia 90–95 × 36–40 μ. Pseudoparaphyses 90–100 μ: longest 150 μ. Total length to tip of perithecium 300 μ: greatest width 45 μ.

On *Bembidium* sp., Maine.

Allied to *L. vulgaris*, from which it is distinguished by its slender, elongate, cylindrical basal cells, and by its inflated, pointed perithecium, which is also differently situated in relation to the insertion of the pseudoparaphyses.

LABOULBENIA VULGARIS, Peyr.

A form referable to this species, and occurring on the elytra of species of Bembidium, has been received from Washington on hosts collected by Miss Parker, and is also not uncommon on Bembidia taken in Maine. The figures and description given by Peyritsch leave much to be desired, yet the determination seems tolerably certain.

LABOULBENIA NEBRIÆ, Peyr.

This well marked form can hardly be confused with any other described species, and is very common on *Nebria pallipes* in Connecticut, covering all parts of the host with a furry mass of individuals. It was accidentally omitted from my previous note, though incidentally referred to.

LABOULBENIA TRUNCATA, Thaxter.

Additional material of this species shows that in perfect and mature specimens the inner pseudoparaphysis develops a long branch, which extends nearly at right angles to the axis of the perithecium, and to a considerable distance beyond it, thus presenting a very characteristic appearance. The species has been received on various species of Bembidium from Virginia (Pergande) and Washington (Miss Parker).

V.

ON A THEOREM OF SYLVESTER'S RELATING TO NON-DEGENERATE[*] MATRICES.

By HENRY TABER, CLARK UNIVERSITY.

Presented March 9, 1892.

IN his *Memoir on Matrices,* Cayley enunciated the theorem that the most general matrix commutative with a given matrix was a rational integral function of it. Of this theorem Sylvester gave a proof, in the Johns Hopkins University Circulars, Vol. III. pp. 34 and 57, for the case in which the latent roots of the given matrix were all distinct, but pointed out that, when the latent roots of the given matrix were not all distinct, the theorem did not always hold. Subsequently, in the Comptes Rendus, Vol. XCVIII. p. 471, Sylvester stated that he had proved that Cayley's theorem held for a matrix of the third order which was not degenerate (*dérogatoire*),[†] irrespective of equalities between its latent roots; and he further stated that Cayley's theorem was probably true for non-degenerate matrices of any order; i. e. that the most general matrix commutative with a non-degenerate matrix of any order whatever was a rational integral function of it. I shall in this paper verify this conjecture of Sylvester's. The theorem follows very simply from one given by the author in a note in these Proceedings for May 26, 1891,[‡] which contains the complete solution of the problem to find the most general matrix commutative with a given matrix.

The theorem is then to be proved for the case in which the latent roots of the given matrix are not all distinct. If the distinct latent roots of the given matrix Ω are g_1, g_2, g_3, etc., of multiplicity

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[*] Sylvester employs the term *matrice dérogatoire* (Comptes Rendus, Vol. XCVIII. p. 471) to denote a matrix whose identical equation is of order lower than the order of the matrix; such a matrix I term a *degenerate* matrix.

[†] See preceding note.

[‡] These Proceedings, Vol. XXVI. p 64.

m, n, p, etc., respectively, then Ω may be written as $\omega\theta\omega^{-1}$, where ω is a non-vacuous matrix, and

$$\theta = \left(\begin{array}{cccc} \boxed{\theta_1} & & & \\ & \boxed{\theta_2} & & \\ & & \boxed{\theta_3} & \\ & & & \ddots \end{array}\right),$$

in which all the constituents are zero except those in the squares θ_1, θ_2, θ_3, etc., along the principal diagonal; these correspond respectively to the latent roots g_1, g_2, g_3, etc., and are subsidiary matrices each of order equal to the multiplicity of the respective latent root to which it corresponds. Since Ω is supposed non-degenerate, the characteristics of its latent roots are $(m;\ 1, 1, \ldots . 1)$, $(n;\ 1, 1, \ldots . 1)$, $(p;\ 1, 1, \ldots . 1)$, etc., respectively. Moreover, since the characteristics of g_1 are $(m;\ 1, 1, \ldots . 1)$,

$$\theta_1 = \left.\overbrace{\left|\begin{array}{cccccc} g_1 & 1 & 0 & 0 & 0 & \cdots \\ 0 & g_1 & 1 & 0 & 0 & \cdots \\ 0 & 0 & g_1 & 1 & 0 & \cdots \\ 0 & 0 & 0 & g_1 & 1 & \cdots \\ 0 & 0 & 0 & 0 & g_1 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{array}\right|}^{m}\right\} m$$

In like manner, in the subsidiary matrix θ_2 the principal diagonal is bordered on the right by unity, and the constituents in the principal diagonal are all equal to g_2, the remaining $m^2 - 2m + 1$ constituents being zero; similarly with respect to the remaining squares, θ_3, etc.

Let ϑ_1, ϑ_2, etc., denote the matrices obtained from θ by erasing successively all the constituents of θ except, first, those in the square θ_1; second, those in the square θ_2, etc. Then

$$\theta = \vartheta_1 + \vartheta_2 + \vartheta_3 + \cdots ;$$

and since the ϑ's are nilfactorial together, i. e. since $\vartheta_1 \vartheta_2 = \vartheta_2 \vartheta_1 = 0$, etc., therefore

$$\theta^2 = \vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2 + \cdots\cdot,$$

$$\theta^3 = \vartheta_1^3 + \vartheta_2^3 + \vartheta_3^3 + \cdots\cdot,$$

etc., etc.

Consequently, if $\boldsymbol{f}(\theta)$ is any rational integral function of θ of which k is the term independent of θ, and if $f(\theta) = \boldsymbol{f}(\theta) - k$, then

$$\boldsymbol{f}(\theta) = f(\theta) + k = f(\vartheta_1) + f(\vartheta_2) + f(\vartheta_3) + \cdots\cdot + k.$$

Let $[r, s]$ denote the matrix whose constituents are all zero except that in the r-th row and s-th column, which is unity. We have then

$$\vartheta_1 = g_1 \Sigma_{1r}^{m} [r, r] + \Sigma_{1\ r}^{m-1} [r, r + 1],$$

$$\vartheta_2 = g_2 \Sigma_{1r}^{n} [m + r, m + r] + \Sigma_{1\ r}^{n-1} [m + r, m + r + 1],$$

$$\vartheta_3 = g_3 \Sigma_{1r}^{p} [m+n+r, m+n+r] + \Sigma_{1\ r}^{p-1} [m+n+r, m+n+r+1],$$

etc., etc.

By the laws of multiplication of the symbols $[r, s]$, viz.

$$[r, s]\,[s, t] = [r, t], \qquad [r, s]\,[t, v] = 0 \;(s \neq t),$$

it follows that

$$\vartheta_1^2 = g_1^2 \Sigma_{1r}^{m} [r, r] + 2\, g_1 \Sigma_{1\ r}^{m-1} [r, r + 1] + \Sigma_{1\ r}^{m-2} [r, r + 2],$$

$$\vartheta_1^3 = g_1^3 \Sigma_{1r}^{m} [r, r] + 3\, g_1^2 \Sigma_{1\ r}^{m-1} [r, r + 1] + 3\, g_1 \Sigma_{1\ r}^{m-2} [r, r + 2] + \Sigma_{1\ r}^{m-3} [r, r + 3],$$

. . . .

$$\vartheta_1^{\mu} = g_1^{\mu} \Sigma_{1r}^{m} [r, r] + \frac{d}{d g_1} g_1^{\mu} \Sigma_1^{m-1} [r, r+1] + \frac{1}{2} \frac{d^2}{d g_1^2} g_1^{\mu} \Sigma_1^{m-2} [r, r+2] + \cdots\cdot + \frac{1}{(m-1)\,!} \frac{d^{m-1}}{d\, g_1^{m-1}} g_1^{\mu} [1, m].$$

Therefore, if $f'(g)$, $f''(g)$, etc., denote respectively the first, second, etc., differential coefficients of $f(g)$ with respect to g, then

$$f(\vartheta_1) = f(g_1)\,\Sigma_{1\,r}^{\,m}[r, r] + f'(g_1)\,\Sigma_{1\,r}^{\,m-1}[r, r+1] + \frac{f''(g_1)}{2}\,\Sigma_{1\,r}^{\,m-2}[r, r+2]$$

$$+ \frac{f'''(g_1)}{2.3}\,\Sigma_{1\,r}^{\,m-3}[r, r+3] + \cdots\cdots + \frac{f^{(m-1)}(g_1)}{(m-1)\,!}[1, m]$$

$$= \Sigma_{0\,s}^{\,m-1}\left\{\frac{f^{(s)}(g_1)}{s\,!}\,\Sigma_{1\,r}^{\,m-s}[r, r+s]\right\},$$

Similarly, we have

$$f(\vartheta_2) = f(g_2)\,\Sigma_{1r}^{\,n}[m+r, m+r] + f'(g_2)\,\Sigma_{1r}^{\,n}[m+r, m+r+1]$$

$$+ \frac{f''(g_2)}{2}\,\Sigma_{1\,r}^{\,n-2}[m+r, m+r+2] + \cdots\cdots + \frac{f^{(n-1)}(g_2)}{(n-1)\,!}[m+1, m+n]$$

$$= \Sigma_{0\,s}^{\,n-1}\left\{\frac{f^{(s)}(g_2)}{s\,!}\,\Sigma_{1\,r}^{\,n-s}[m+r, m+r+s]\right\},$$

$$f(\vartheta_3) = f(g_3)\,\Sigma_{1}^{\,p}[m+n+r, m+n+r]$$

$$+ f'(g_3)\,\Sigma_{1\,r}^{\,p-1}[m+n+r, m+n+r+1]$$

$$+ \frac{f''(g_3)}{2}\,\Sigma_{1\,r}^{\,p-2}[m+n+r, m+n+r+2] + \cdots\cdots$$

$$+ \frac{f^{(p-1)}(g_3)}{(p-1)\,!}[m+n+1, m+n+p]$$

$$= \Sigma_{0\,s}^{\,p-1}\left\{\frac{f^{(s)}(g_3)}{s\,!}\,\Sigma_{1\,r}^{\,p-s}[m+n+r, m+n+r+s]\right\},$$

etc., etc.

And since $\boldsymbol{f}'(g) = f'(g)$, $\boldsymbol{f}''(g) = f''(g)$, etc., and

$$1 = \Sigma_{1r}^{\,m}[r, r\rfloor + \Sigma_{1r}^{\,n}[m+r, m+r]$$

$$+ \Sigma_{1r}^{\,p}[m+n+r, m+n+r] + \cdots\cdots,$$

it follows that

$$\boldsymbol{f}(\theta) = f(\theta) + k$$

$$= f(\vartheta_1) + f(\vartheta_2) + f(\vartheta_3) + \cdots\cdots + k$$

$$= \Sigma_{0\,s}^{\,m-1}\left\{\frac{\boldsymbol{f}^{(s)}(g_1)}{s\,!}\,\Sigma_{1r}^{\,m}[r, r+s]\right\}$$

$$+ \Sigma_{0\,s}^{\,n-1}\left\{\frac{\boldsymbol{f}^{(s)}(g_2)}{s\,!}\,\Sigma_{1r}^{\,n}[m+r, m+r+s]\right\}$$

$$+ \Sigma_{0\,s}^{\,p-1}\left\{\frac{\boldsymbol{f}^{(s)}(g_3)}{s\,!}\,\Sigma_{1r}^{\,p}[m+n+r, m+n+r+s]\right\} + \text{etc.}$$

Let now

$$f_1(\theta) = [(\theta - g_1)^m - (g_2 - g_1)^m]^n\,[(\theta - g_1)^m - (g_3 - g_1)^m]^p \ldots\ldots,$$

the remaining factors corresponding to the remaining latent roots; then for $g = g_1$,

$$f_1(g) = f_1(g_1) \neq 0,\; f_1'(g) = 0,\; f_1''(g) = 0,\; \ldots\ldots f_1^{(m-1)}(g) = 0;$$

for $g = g_2$, $f_1(g) = 0$, and likewise its first $n - 1$ differential coefficients; similarly, for $g = g_3$, $f_1(g)$ and its first $p - 1$ differential coefficients are all zero, etc. Therefore

$$\frac{f_1(\theta)}{f_1(g_1)} = \Sigma_{1\,r}^{\,m}\,[r,\, r].$$

It may be shown in like manner that

$$\frac{f_1(\theta)}{f_1(g_1)}\,(\theta - g_1) = \Sigma_{1\,r}^{\,m-1}\,[r,\, r + 1],$$

$$\frac{f_1(\theta)}{f_1(g_1)}\,(\theta - g_1)^2 = \Sigma_{1\,r}^{\,m-2}\,[r,\, r + 2],$$

. . . .

$$\frac{f_1(\theta)}{f_1(g_1)}\,(\theta - g_1)^{m-1} = [1,\, m].$$

Similarly, if

$$f_2(\theta) = [(\theta - g_2)^n - (g_1 - g_2)^n]^m\,[(\theta - g_2)^n - (g_3 - g_2)^n]^p \ldots\ldots,$$

then it may be shown in like manner that

$$\frac{f_2(\theta)}{f_2(g_2)} = \Sigma_{1\,r}^{\,n}\,[m + r,\, m + r],$$

$$\frac{f_2(\theta)}{f_2(g_2)}\,(\theta - g_2) = \Sigma_{1\,r}^{\,n-1}\,[m + r,\, m + r + 1],$$

$$\frac{f_2(\theta)}{f_2(g_2)}\,(\theta - g_2)^2 = \Sigma_{1\,r}^{\,n-2}\,[m + r,\, m + r + 2],$$

. . . .

$$\frac{f_2(\theta)}{f_2(g_2)}\,(\theta - g_2)^{n-1} = [m + 1,\, m + n],$$

etc., etc.

Now, by reference to the theorem referred to above, it will be seen that if ϕ is the most general matrix commutative with Ω, then ϕ may be written as $\omega \, \eta \, \omega^{-1}$ where

$$\eta = \left(\begin{array}{cccc} \boxed{\eta_1} & & & \\ & \boxed{\eta_2} & & \\ & & \boxed{\eta_3} & \\ & & & \ddots \end{array} \right),$$

in which all the constituents are zero except those in the squares η_1, η_2, etc., along the principal diagonal, and these square arrays or subsidiary matrices are of order equal respectively to the order of the subsidiary matrices θ_1, θ_2, etc., to which they severally correspond; moreover,

$$\eta_1 = \left. \overbrace{\boxed{\begin{array}{cccccc} a_1 & b_1 & c_1 & d_1 & e_1 & \cdots \\ 0 & a_1 & b_1 & c_1 & d_1 & \cdots \\ 0 & 0 & a_1 & b_1 & c_1 & \cdots \\ 0 & 0 & 0 & a_1 & b_1 & \cdots \\ 0 & 0 & 0 & 0 & a_1 & \cdots \\ \text{etc.} & \cdots & \cdots & \cdots & \cdots & \cdots \end{array}}}^{m} \right\} m$$

$$\eta_2 = \left. \overbrace{\boxed{\begin{array}{cccccc} a_2 & b_2 & c_2 & d_2 & e_2 & \cdots \\ 0 & a_2 & b_2 & c_2 & d_2 & \cdots \\ 0 & 0 & a_2 & b_2 & c_2 & \cdots \\ 0 & 0 & 0 & a_2 & b_2 & \cdots \\ 0 & 0 & 0 & 0 & a_2 & \cdots \\ \text{etc.} & \cdots & \cdots & \cdots & \cdots & \cdots \end{array}}}^{n} \right\} n$$

etc., etc.

Therefore, if ϵ_1, ϵ_2, etc., severally denote the matrices formed from η by erasing successively all its constituents except, first, those in the square η_1, second, those in the square η_2, etc., then

$$\eta = \epsilon_1 + \epsilon_2 + \cdots\cdot,$$

and

$$\epsilon_1 = a_1 \Sigma_1{}^{m}_{r} \left[r,\ r\right] + b_1 \Sigma_1{}^{m-1}_{r} \left[r,\ r+1\right] + c_1 \Sigma_1{}^{m-2}_{r} \left[r,\ r+2\right] \\ + d_1 \Sigma_1{}^{m-3}_{r} \left[r,\ r+3\right] + e_1 \Sigma_1{}^{m-4}_{r} \left[r,\ r+4\right] + \cdots\cdot$$

$$\epsilon_2 = a_2 \Sigma_1{}^{n}_{r} \left[m+r,\ m+r\right] + b_2 \Sigma_1{}^{n-1}_{r} \left[m+r,\ m+r+1\right] \\ + c_2 \Sigma_1{}^{n-2}_{r} \left[m+r,\ m+r+2\right] + d_2 \Sigma_1{}^{n-3}_{r} \left[m+r,\ m+r+3\right] \\ + e_2 \Sigma_1{}^{n-4}_{r} \left[m+r,\ m+r+4\right] + \cdots\cdot,$$

etc., etc.

But by what has just been proved it follows that

$$\epsilon_1 = \frac{f_1(\theta)}{\dot{f}_1(g_1)} \{a_1 + b_1(\theta - g_1) + c_1(\theta - g_1)^2 + d_1(\theta - g_1)^3 + e_1(\theta - g_1)^4 + \cdots\cdot\},$$

$$\epsilon_2 = \frac{f_2(\theta)}{\dot{f}_2(g_2)} \{a_2 + b_2(\theta - g_2) + c_2(\theta - g_2)^2 + d_2(\theta - g_2)^3 + e_2(\theta - g_2)^4 + \cdots\cdot\},$$

etc. Consequently η is a rational integral function of θ. Let $\eta = f(\theta)$, where $f(\theta)$ denotes the most general rational integral function of θ; then, since

$$\omega \cdot f(\theta) \cdot \omega^{-1} = f(\Omega),$$

the most general matrix commutative with Ω is

$$\phi = \omega\, \eta\, \omega^{-1} = \omega \cdot f(\theta) \cdot \omega^{-1} = f(\Omega).$$

WORCESTER, MASS., January 2, 1892.

POSTSCRIPT.

WORCESTER, MASS., March 26, 1892.

I find that the solution of the matrical equation $\Omega\phi = \phi\Omega$ given in a note in these Proceedings, May 26, 1891, and upon which the proof of the theorem given above is based, gives the complete solution of the more general matrical equation $\Omega\phi = \phi\Omega'$ for that case in which it may be assumed that the determinant of ϕ is not null. For this case the latent roots of Ω' are identical with those of Ω, and have, respectively, the same characteristics, i. e. the nullities of successive powers of Ω' less any latent root g are respectively equal to the nullities of successive powers of $\Omega - g$. Therefore, if the canonical form of Ω is $\omega\,\theta\,\omega^{-1}$, the canonical form of Ω' is $\omega'\,\theta\,\omega'^{-1}$.* Matrices thus related are termed by Weyr matrices of the same kind.

If, then, in the equation

$$\Omega\phi = \phi\Omega',$$

Ω and Ω' are replaced by their equivalents, it becomes

$$\omega\,\theta\,\omega^{-1}\phi = \phi\,\omega'\,\theta\,\omega'^{-1},$$

that is,

$$\theta\,.\,\omega^{-1}\phi\,\omega' = \omega^{-1}\phi\,\omega'\,.\,\theta.$$

If, now, we put

$$\psi = \omega^{-1}\phi\,\omega',$$

the equation becomes

$$\theta\psi = \psi\theta.$$

But the most general solution of this equation is given in the note above referred to; the most general matrix commutative with θ is there denoted by η. Therefore, the most general solution of the matrical equation

$$\phi\,\Omega = \Omega'\phi$$

is

$$\phi = \omega\,\psi\,\omega'^{-1},$$

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* For explanation of the term canonical form of a matrix, see paper referred to, these Proceedings, Vol. XXVI. p. 64.

if the canonical forms of Ω and Ω' are respectively $\omega\,\theta\,\omega^{-1}$ and $\omega'\,\theta\,\omega'^{-1}$, and provided ψ is the most general matrix commutative with θ.

This solution of the equation $\Omega\,\phi = \phi\,\Omega'$, as also the above mentioned solution of the equation $\Omega\,\phi = \phi\,\Omega$, depends upon the reduction of a matrix to its canonical form. In the assumed canonical form of Ω, viz. $\omega\,\theta\,\omega^{-1}$, the matrix θ is dependent solely upon the characteristics of the latent roots of Ω. Having determined the latent roots of Ω and their characteristics, if one value of ω is known, the solution of the preceding equation $\Omega\,\phi = \phi\,\Omega'$ gives in terms of ω every solution of the problem to reduce a given matrix Ω to its canonical form. For if $\Omega' = \theta$, the most general solution of the equation

$$\Omega\,\phi = \phi\,\Omega'$$

reduces to

$$\phi = \omega\,\psi,$$

where ψ is the most general matrix commutative with θ, and ω is some particular value of ϕ satisfying the equation $\Omega = \phi\,\theta\,\phi^{-1}$. But since the solutions of this equation are all included in those of the equation $\Omega\,\phi = \phi\,\theta$, if the constants in ψ are so taken that its determinant (and consequently the determinant of ϕ) is not null, $\phi = \omega\,\psi$ is the most general solution of the problem to reduce a matrix to its canonical form.

If Ω and Ω' are matrices of the same kind,* and such that for any latent root g the increments of nullity of successive powers of $\Omega - g$ (or $\Omega' - g$) are severally equal to the nullity of $\Omega - g$ (or of $\Omega' - g$), until a power is reached whose nullity is equal to its vacuity, then the most general solution of the equation $\Omega\,\phi = \phi\,\Omega'$ can be expressed in terms of certain arbitrary matrices and of products of powers of Ω and Ω' less their latent roots. Thus, let the latent roots of Ω (and of Ω') be g_1, g_2, ... g_i, respectively of multiplicity m_1, m_2, ... m_i; and suppose that the nullities of $\Omega - g_1$, $\Omega - g_2$, etc. are m'_1, m'_2, etc. From the supposed equality in the increments of nullity of $\Omega - g_1$, etc., it follows that

$$\mu_1 = \frac{m_1}{m'_1}, \quad \mu_2 = \frac{m_2}{m'_2}, \quad \ldots . \; \mu_i = \frac{m_i}{m'_i},$$

are all integers. Let, now,

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* That is, Ω and Ω' are such that it is possible to find a matrix χ to satisfy the equation $\Omega' = \chi\,\Omega\,\chi^{-1}$.

$$f_r(g) \equiv (\overline{g - g_r}^{\mu_r} - \overline{g_1 - g_r}^{\mu_r})^{\alpha_1} (\overline{g - g_r}^{\mu_r} - \overline{g_2 - g_r}^{\mu_r})^{\mu_2} \ldots\ldots$$
$$(\overline{g - g_r}^{\mu_r} - \overline{g_{r-1} - g_r})^{\mu_{r-1}} (\overline{g - g_r}^{\mu_r} - \overline{g_{r+1} - g_r}^{\mu_r})^{\mu_{r+1}} \ldots\ldots$$
$$(\overline{g - g_r}^{\mu_r} - \overline{g_i - g_r}^{\mu_r})^{\mu_i},$$

$$\Omega_r = \frac{f_r(\Omega)}{f_r(g_r)}, \qquad \Omega'_r = \frac{f_r(\Omega')}{f_r(g_r)}.$$

Then the most general expression for the matrix ϕ satisfying the equation $\Omega\,\phi = \phi\,\Omega'$ is

$$\phi = \Sigma_{0\,r}^{\mu_1 - 1}\{(\Omega - g_1)^{\mu_1 - r - 1}\,\Omega_1\,\mathrm{M}_1\,\Omega'_1\,(\Omega' - g_1)^r\}$$
$$+ \Sigma_{0\,r}^{\mu_2 - 1}\{(\Omega - g_2)^{\mu_2 - r - 1}\,\Omega_2\,\mathrm{M}_2\,\Omega'_2\,(\Omega' - g_2)^r\}$$
$$+ \ldots\ldots + \Sigma_{0\,r}^{\mu_i - 1}\{(\Omega - g_i)^{\mu_i - r - 1}\,\Omega_i\,\mathrm{M}\,\Omega'_i\,(\Omega' - g_i)_r\},$$

where M_1, M_2, ... M_i, are arbitrary matrices.

If $\Omega' = \Omega$, the expression to which this expression for ϕ reduces gives the most general matrix commutative with Ω.

If $\Omega' = \theta$, and the matrices M in the above expression for ϕ are so taken (as is possible) that the determinant of ϕ is not null, then the expression for ϕ gives the most general solution of the reduction of the given matrix Ω to its canonical form.

VI.

RESEARCHES ON THE VOLATILE HYDROCARBONS.

By C. M. Warren.

Communicated May 12, 1868.*

III.—ON THE VOLATILE HYDROCARBONS IN PENNSYLVANIA PETROLEUM.—Part I.

The results recorded in this paper were obtained previously to the publication of a memoir "On the Influence of CH_2 on the Boiling-points in Homologous Series of Hydrocarbons," etc., which I had the honor to present to the Academy in 1864.† In that memoir I had occasion, for a special purpose, to introduce, among others, the formulæ of the hydrocarbons that I had separated from Pennsylvania petroleum, but omitting for the time being the data from which these formulæ were deduced, with the intention to follow shortly after with another paper in which these data would be given. Publication was at first delayed for an opportunity to repeat some of the analyses by means of my process for combustion in oxygen gas,‡ (which is specially suited to the analysis of volatile substances,) with the view to obtain more exact results which might throw some light on the question raised in that paper,* as to whether the 1st and 2d series there presented should be considered isomeric. For the same reason, it seemed desirable also, before publication, that the relations of these series should be further studied by at least a preliminary examination of some of the more important chemical properties of the different bodies which they comprise. With no immediate prospect of being able to pursue these inquiries,—already so long deferred from unavoidable causes,—it seems now advisable to publish the results obtained, without relinquishing, however, the hope of continuing the investigation.

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* The manuscript of this memoir was found among the author's papers after his death. The article had been presented to the Academy by title at a meeting held on May 12, 1868, and appears to have been written out in its present shape at that time, with the possible exceptions that one or two brief footnotes may have been added subsequently, and that the style of naming some of the compounds may have been changed. The author's motive for holding back the communication — as indicated by brief marginal notes written in pencil upon his manuscript — seems to have been based on a wish to make one or two new analyses, and to repeat by a process of his invention a few determinations of vapor density, in order that absolute justice might be done to Pelouze and Cahours in his criticism of their work. Broadly considered, the delay appears to have been a case of procrastination pure and simple, for there is evidence that the author had never given up his intention of publishing the paper as it now stands.

† Memoirs of the American Academy, (N. S.) IX. 156.

‡ Proceedings of the American Academy, 1864, p. 251.

Notwithstanding the fact, as above intimated, that some of the results to be presented are not entirely satisfactory, they are published in the belief that they are more nearly correct than the corresponding results that others have obtained in the investigation of this petroleum; and will, therefore, contribute materially to our knowledge of the bodies obtained therefrom. This belief is justified by the circumstance that the different constituents of the petroleum were separated by a process far more searching and reliable than any distillatory process that had been applied to such a mixture; † hence, that the several bodies examined were obtained in a state approximating much nearer to purity than seems possible by any other method of fractional distillation yet devised. As a natural consequence, some of the more important results that I have obtained in the study of this petroleum differ essentially from those of other investigators of the same material, notably those of Pelouze and Cahours, whose researches are often quoted as authority on this subject.‡

Before proceeding to give the experimental results which it is the special object of this paper to furnish, it may be of service, and may excite additional interest in the subject, to recall briefly some of the facts furnished in my former paper, and to specify some of the more striking differences between my results and those of the chemists above mentioned.

In the memoir first above referred to (pp. 166, 167), the hydrocarbons that I have separated from this petroleum are classified in three natural series, designated, provisionally, as 1st, 2d, and 3d series. The first two of these may be conveniently considered as parallel series, since they exist as it were side by side, and in fact extend through and naturally belong to the same portion of the petroleum, and present, moreover, a nearly uniform difference of boiling-point, viz. about 8° C. between any two corresponding or opposite members of the two series, as will appear on inspection of the tables. Both series, however, have in common the boiling-point difference of about 30° between any two contiguous members, corresponding to the common elementary difference of $\text{€}H_2$, as also shown in the tables referred to. The members of the 3d series have boiling-points ranging from 0° to 150°, and those of the 2d series from about 8° to 128°.

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* See foot-note, page 167.

† "Process of Fractional Condensation," etc., Memoirs of the American Academy, (N. S.) IX. 121.

‡ Comptes Rendus, LIV. 1241, LVI. 505, LVII. 62.

In striking contrast with these results, Pelouze and Cahours found in this portion of the petroleum but one series, or only about one half the number of bodies that I obtained. We do not differ, however, as to the general formula (€_nH_{2n+2}) of the bodies belonging to this portion of the petroleum. But in regard to the boiling-point difference for the successive terms of the series, which, as already stated, I have shown to be uniformly about 30° in the €_nH_{2n+2} Series, we find in their results hardly an approximation to uniformity in this respect. On the contrary, their boiling-point differences, corresponding to an elementary difference of $\text{€}H_2$, are observed to vary so widely as from 16° or 20° to 38°.

Yet more remarkable is the circumstance that, above 150° (the highest point reached by either of my first two series), in that part of the petroleum embracing my 3d series, in which I find only bodies of the general formula €_nH_{2n}, they find, on the contrary, none of these, but continue to obtain bodies which they represent as having the same general formula as those belonging to the more volatile portion of the petroleum.* They maintain that the whole liquid portion of the petroleum is made up of one continuous series, having the general formula $Ꞓ_nH_{2n+2}$; and, moreover, that the solid paraffines from this source belong also to this series, of which at least there is much reason to doubt.

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* The temperatures here given relate, of course, either to isolated substances, or to sections of the petroleum considered as if composed exclusively of those bodies whose true boiling points have been found to come within the limits of temperature above indicated; not ignoring the fact, however, that during the process of separation, when applied to a mixture that includes all of the three series, some of the 1st and 2d series come off in reality at temperatures considerably above that indicated as the highest limit of these two series, viz. 150°; nor unmindful of the fact, on the other hand, that some of those of higher boiling-point — members of the 3d series — are carried over with the

Concerning a natural product of great importance in itself and in its relations, results so discordant as above indicated should have a careful and impartial examination with reference to the different conditions under which they were respectively obtained, with the view to determine which should be regarded as the more accurate. Having this purpose in view, and with the conviction that the work done does not so much need repetition as to be understood, and believing that the facts that I have to present are sufficient to establish at least the probability of the correctness of the conclusions I have reached, it will be necessary, in the following consideration of the subject, to make such further comparison of their results with my own as the pursuit of the object defined seems to require.

EXAMINATION OF THE PETROLEUM.

Of the Material employed.—Commercial Products from the Petroleum.

In the investigation of this petroleum I have not operated directly on the crude oil, but upon certain distillates obtained from this on a manufacturing scale. Special care was taken to procure these from a reliable source, and to obtain such as had not been subjected to any chemical treatment; and also such, taken collectively, as would fairly represent the natural product so far as to include in sufficient quantity all of its constituents. A brief description of these crude distillates, indicating their comparative value as sources of supply of the different constituents, may not be void of interest, and may be of service to such, especially, as may have occasion to repeat any portion of the work. This remark is suggested by a statement of Schorlemmer[*] with respect to one of the members of my 1st series, viz. that boiling at 61°.3, that it was not present in the petroleum that he worked upon. After the

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vapors of the more volatile ones, at temperatures below their true boiling-points, or within the range of the 1st and 2d series, their true or natural position in the series not admitting of determination until, by the process of separation, the bodies shall have attained a comparatively high degree of purity.

[*] Philosophical Transactions, 1872, Vol. CLXII. p. 116.

publication of my first memoir, above referred to, this chemist appears to have made a special search for these bodies, which were entirely overlooked in his earlier research, and such of them as he found he seems to have obtained in small proportion,— quite the reverse of my experience. E. g., of the body boiling at 61°.3, which, as stated, he did not find, the proportion of my product, as compared with that boiling at about 68°, was as 7 to 8.

In the earlier stage of the distillation, in the manufacture of "illuminating oil" or "refined petroleum," (a medium product, amounting to some 70 per cent of the crude material,) there is obtained, as is well known, a considerable quantity — frequently about 15 per cent — of a colorless and highly volatile liquid, variously known in commerce as naphtha, spirits of petroleum, and, improperly, as benzine. Although containing some of the substances that more especially characterize the heavier or medium portion of the petroleum, the larger proportion of this naphtha is composed of bodies whose boiling-points range from 0° to 150°, these being the limits of my provisional 1st and 2d series, and is therefore a convenient source from which these for the most part may be obtained. Some manufacturers separate this naphtha, either by a second distillation or during the distillation of the crude petroleum, into two parts, a "light" and a "heavy naphtha." The former of these is the product commercially known in the United States as "Gasolene," which is more or less extensively employed, mixed as vapor with atmospheric air, as a substitute for coal gas. It was from this "gasolene" or "light naphtha," having the specific gravity 0.65 at 15° C, that the hydrocarbons comprised in my 1st and 2d series were chiefly procured. Although this product contains a larger proportion of some of the lower or medium members of these two series,— as its low specific gravity and high degree of volatility would indicate,— it also contains considerable quantities of the higher ones; but the latter may be obtained in greater abundance from the "heavy naphtha," and in notable quantity also from the medium product described as "illuminating oil," from which to a considerable extent it may be conveniently procured while operating to obtain the members of the 3d series, of which this product is chiefly composed.

In the manufacture of these naphthas, a large portion of the two most volatile constituents of the petroleum — those boiling at 0° and 8° respectively — is generally allowed to escape condensation, and to a considerable extent, also, the two next higher ones, boiling at 30° and 38°. Since the first two here mentioned, when isolated from those of higher boiling-points, are gases at the common temperature, a mixture of these may be more readily obtained in large quantity from a manufactory, by conducting the vapors from the still into a condenser maintained at a low temperature, — being the product introduced by Dr. Henry J. Bigelow for a local anæsthetic under the name of Rhigolene.* The large preponderance, in this product, of these most volatile constituents of the petroleum might be inferred from the fact, as stated by him, that when continuously dropped on the bulb of a mercurial thermometer evaporation is so rapid as to cause the mercury to fall to —7° within 5 to 10 seconds.

Of the Results of Fractional Condensation.

For convenience of reference I will here repeat, with slight modifications, some of the tables from my previous memoir. These exhibit the three homologous series of hydrocarbons that I have separated from the petroleum, together with their boiling-points, the differences of boiling-point corresponding to an elementary difference of $ꞒH_2$, and their formulæ, — the data for which are given on the following pages.

Hydrocarbons from Pennsylvania Petroleum.

1. MARSH-GAS SERIES.

Name of Substance.	Formula. $Ꞓ_nH_{2n+2}$	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
		°		°	°
Butyl Hydride	$Ꞓ_4H_{10}$	0.0 †	—	—	—
Amyl "	$Ꞓ_5H_{12}$	30.2	$ꞒH_2$	30.2	1.5
Hexyl "	$Ꞓ_6H_{14}$	61.3	$ꞒH_2$	31.1	0.8
Heptyl "	$Ꞓ_7H_{16}$	90.4	$ꞒH_2$	29.1	1.0
Octyl "	$Ꞓ_8H_{18}$	119.5	$ꞒH_2$	29.1	1.0
Nonyl "	$Ꞓ_9H_{20}$	150.8	$ꞒH_2$	31.3	0.8

150.8 ÷ 5 = 30°.16

Average increment of boiling-point for the addition of CH_2 = 30°.16.

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* Chemical News, 1866, XIII. 244.

† Ronald's determination.

2. ISOMERIC (?) WITH THE MARSH-GAS SERIES.

Name of Substance.	Formula. $Ȼ_nH_{2n+2}$	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
Iso-Butyl Hydride	$Ȼ_4H_{10}$	° 8–9	—	° —	° —
“ Amyl “	$Ȼ_5H_{12}$	37.0	$ȻH_2$	29.0	0.4
“ Hexyl “	$Ȼ_6H_{14}$	68.5	$ȻH_2$	31.5	0.6
“ Heptyl “	$Ȼ_7H_{16}$	98.1	$ȻH_2$	29.6	1.2
“ Octyl “	$Ȼ_8H_{18}$	127.6	$ȻH_2$	29.5	1.5

119.6 ÷ 4 = 29°.9

Average increment of boiling-point for the addition of CH_2 = 29°.9.

3. ETHYLENE SERIES.

Name of Substance.	Formula. $Ȼ_nH_{2n}$	Boiling-point.	Elementary Difference.	Difference of Boiling-point found.	Range of Temperature within which Substance all distilled.
Rutylene	$Ȼ_{10}H_{20}$	° 174.9	—	° —	° 1.7
Margarylene	$Ȼ_{11}H_{22}$	195.8	$ȻH_2$	20.9	1.5
Laurylene	$Ȼ_{12}H_{24}$	216.2	$ȻH_2$	20.3	2.2

41.2 ÷ 2 = 20°.6

Average increment of boiling-point for the addition of CH_2 = 20°.6.

Having already given in one of the memoirs above referred to a detailed description of the process devised for the separation of the constituents of such complex mixtures of liquids as that under consideration, and which was employed in this research, these details are here omitted. I should state, however, that in conducting the separations in this case, the same exhaustive method was pursued as therein described.* By this treatment, the intermediate small fractions lying between the prominent ones were repeatedly and so thoroughly worked over as to prove the absence of other bodies than those described, i. e. in quantities appreciable by fractional condensation. I do not, however, ignore the fact that small quantities of other bodies might be present and escape detection. That any appreciable constituent of that part of the petroleum worked upon was overlooked in this investigation is the more improbable from the fact that, in consequence of the discovery of the new series isomeric with the hydrides, vastly more time and labor were given to these separations than are ordinarily required, or than would have been necessary otherwise. The extremely small difference of boiling-point between the corresponding or opposite members of these two parallel series has necessitated a most thorough and critical examination, requiring a vast number of redistillations, each extending over the whole range of fractions,— a fraction being taken for every degree of temperature,— and this extremely tedious process was continued until the small intermediate fractions, as before stated, had become too small to admit of being further operated upon; and until the boiling temperature of the large fractions herein treated of had ceased to undergo further change by this treatment. This course was deemed indispensable, — regardless of the large expenditure of time involved,— since nothing less could suffice to remove all doubt as to the existence of the newly discovered series, and insure for the different substances that degree of purity requisite for any satisfactory study of their individual properties.

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* Memoirs of the American Academy, (N. S.) IX. 130–134.

I have laid special stress on the circumstance here related, since it appears, on comparison of my results with those of Pelouze and Cahours, that they claim to have found one more body between about 120° and 236° than I have been able to discover. Either I have overlooked in my analysis one constituent of the petroleum between these limits of temperature, or they have described one having no existence therein; in this connection, for obvious reasons, my newly discovered series of isohydrides is of course not taken into account. To facilitate a comparison of their results with my own, as the latter are exhibited in the preceding tables, I will here introduce the following table prepared by me for this purpose.*

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* At this date the nomenclature here employed may appear antiquated; but since this does not affect the intrinsic value of the paper, I have preferred to let it pass through the press as written several years ago.

Tabular Statement of the Formulæ and Boiling-points of the Constituents of Pennsylvania Petroleum, as determined by Pelouze and Cahours.

Name of Substance.		Formula ($Є_nH_{2n+2}$)	Boiling-point.	Elementary Difference.	Difference of Boiling-point found. (Average.)
Hydride of Butyl		$Є_4H_{10}$	° 5–10	—	° —
"	Amyl	$Є_5H_{12}$	30	$ЄH_2$	22.5
"	Caproyl	$Є_6H_{14}$	68	$ЄH_2$	38.0
"	Œnanthyl	$Є_7H_{16}$	92–94	$ЄH_2$	25.0
"	Capryl	$Є_8H_{18}$	116–118	$ЄH_2$	24.0
"	Pelargonyl	$Є_9H_{20}$	136–138	$ЄH_2$	20.0
"	Rutyl	$Є_{10}H_{22}$	160–162	$ЄH_2$	24.0
"	——	$Є_{11}H_{24}$	180–184	$ЄH_2$	21.0
"	Lauryl	$Є_{12}H_{26}$	196–200	$ЄH_2$	16.0
"	Cocinyl	$Є_{13}H_{28}$	216–218	$ЄH_2$	19.0
"	Myristyl	$Є_{14}H_{30}$	236–240	$ЄH_2$	21.0
"	——	$Є_{15}H_{32}$	255–260	$ЄH_2$	19.5

As their results, indicated by the above table, differ so widely from mine, not only in regard to boiling-points in several instances, but also in the important matters of vapor density and elementary constitution corresponding thereto, as will be shown further on, it is impossible for me to determine with any degree of certainty which of the several bodies they describe should be chosen as the one whose existence in the petroleum must be questioned; for my results, I trust, will show conclusively that one of their number must be discarded, and that consequently the formula of the rejected member would naturally fall to the one next above, and the formula of this in turn to the next higher, and so on, changing the formulæ of all the higher members of their series. Since, however, they have not described a greater number of bodies within the range of temperature embraced by my 3d series — the $Є_nH_{2n}$ series — than were found by me, although we differ widely as to their constitution; and since their boiling-points in this part of the petroleum are less at variance with mine, I am induced to consider that the spurious body in question is more probably one of the two lying between 120° (a point at which we agree very nearly both as to boiling-point and vapor density) and 175°, the point at which my 3d. or $Ꞓ_nH_{2n}$ series, begins. . It matters little which of these it is, and we will therefore assume it to be the lower one of the two, or their first above 120°, viz. that boiling at 136°–138°, which they represent by the formula $Ꞓ_9H_{20}$. This formula, it may be observed, is the same that I have given to a body boiling at about 150°, finding none intermediate between this and 127°; the latter, however, is not of the same series, being isomeric with the body boiling at 120°, having the formula $Ꞓ_8H_{18}$.

The question as to the existence in the petroleum of a body whose boiling-point lies between the limits of temperature indicated, viz. 127° and 150°, is seen to be of more importance when it is considered, as above stated, that it involves the question as to the constitution or correctness of the formula or formulæ of the higher member or members of the series; and especially so if it be held that the $Ꞓ_nH_{2n+2}$ series in petroleum, instead of terminating at 150°, as I maintain, is really so extensive as alleged by Pelouze and Cahours,— they having already assigned to it seven bodies of boiling-points above 118°, the highest of which boils at 260°; and assumed, as already stated, that this series goes on uninterrupted to, and includes, the solid paraffines. For if, as I maintain, the petroleum does not contain the body in question, and if the $Ꞓ_nH_{2n+2}$ series *has* the wide range which they assert, then it must follow that the formulæ assigned by them to these seven or more bodies would each require the deduction of $ꞒH_2$, and hence that their determinations would become almost worthless, since so great a discrepancy would indicate for the substances a degree of impurity sufficient to destroy confidence in the results that they obtained in the further study of these bodies. I have assumed, in this consideration, that the lower members of the series have been correctly determined, there being no disagreement between their determination and my own of the formula — $Ꞓ_8H_{18}$ — of the body boiling at 119°.5 (116°–118° by their determination), nor of the formulæ of the lower members of the series.

Trusting that a comparative examination of the results presented in this paper, giving due consideration to the fact of the greater efficiency of the process employed in my proximate analysis of the petroleum, will leave no room for doubt on the questions presented, and will confirm the views above stated, I will now proceed to give details of the elementary analyses, and of the experiments to determine such of the physical properties of the individual bodies as are usually relied upon to identify or characterize bodies of this class. I would here state, however, once for all, that, unless specially mentioned, no one of the bodies operated upon had received any chemical treatment except that of boiling with sodium.

Of the Analyses and Physical Properties of the different Bodies separated from the Petroleum.

1. BUTYL HYDRIDE AND BUTYL ISO-HYDRIDE = C_4H_{10}.*

My examination of butyl hydride and its isomeric associate in the petroleum has been more limited than that of the other members of the series to which they respectively belong. As these bodies could at any time be readily obtained in larger quantity at a manufactory, in the manner above described, I omitted to make further use of the small quantities that I had incidentally collected than to determine their boiling-points, and of one of them, viz. iso-hydride of butyl, the specific gravity, which was found to be 0.6107 at 0°. Ronalds has found the specific gravity of the other, viz. hydride of butyl, to be 0.600 at 0°.

In the original publication of the above tables, the boiling-point of butyl hydride was given, with an interrogation point, as 0°; for although I had observed that a mixture of the two bodies began to boil at about this temperature, it was on theoretical considerations that this precise figure was given, and, of course, a more positive statement would not be justifiable. That this, however, is at least very nearly its true boiling-point, has since been confirmed by Ronalds,† who has made a special study of the most volatile part of the petroleum, and who states that it begins to boil at 0°. It does not appear, however, that he made a better separation of the two bodies, for he failed even to detect the presence of butyl iso-hydride, and could not therefore have made an attempt to separate it. Moreover, he worked by the old method. Ronalds, however, collected a liquid boiling between 6° and 8°, specific gravity 0.6004, but did not regard it as a distinct body, but merely as a mixture of butyl hydride and amyl hydride, C_5H_{12}, which latter boils at about 30°.

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* Studied in 1868 by E. Lefebvre, Jahresb., 1868, p. 329.

† Journal of the Chemical Society, London, 1865.

It is needless to remark that to call this a mixture, in the broad sense that Ronalds has done, does not accord with my experience. The boiling-point, 8°–9°, that I found for butyl iso-hydride was the result of an actual determination in the usual manner. The material employed for this purpose had been repeatedly and carefully distilled through my regulated condenser; but it had finally become so reduced in quantity as to necessitate suspension of the process of fractionation before the separation was so nearly complete as is claimed for the bodies of higher boiling-point. Nevertheless, it is believed to have been sufficiently pure to justify the conclusion — supported also by analogy — that there is a constituent of the petroleum boiling at about 8° to 9°, as I had stated. I would not, however, be understood to maintain that this body, as obtained, contained no admixture of butyl hydride, or even of amyl hydride, for doubtless it contained both of them to some extent. I only contend that probably neither was present in sufficient quantity to materially, if indeed perceptibly, influence the boiling-point, and consequently that the elevation of the boiling temperature above 0°, or that of butyl hydride, was not due to the presence of amyl hydride, as we should infer from Ronald's statement, but rather to the fact that it was mainly composed of butyl iso-hydride, which he overlooked.

I may remark in this connection that a similar view is held in regard to the purity of the other bodies that I have separated from the petroleum; although the purification of most or many of these was carried to the extreme practicable limit, they doubtless still remained mixtures, but probably in such relative proportions as to admit of correct, or at least very nearly correct, determinations of their boiling-points. That such was the probable condition of these bodies is not merely a theoretical opinion based on my own observations. The experiments of Berthelot * show that mixtures of neutral liquids whose boiling-points differ by 20°–30°, being mixed in such proportion that the least volatile amounts to 8 or 10 per cent, do not admit of separation by distillation under ordinary pressure, and will frequently, if not always, be found to comport themselves like homogeneous substances.

Berthelot's results have since been confirmed by Alluard,† who

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* Comptes Rendus, LVII. 430.

† Comptes Rendus, LVIII. 84.

found that ether mixed with one tenth of its weight of bi-sulphide of carbon, not only had a constant boiling-point, but that this was *the same as that of pure ether.* He also made similar observations on mixtures of bi-sulphide of carbon and alcohol, and alcohol and water.*

In the case of a mixture of two liquid bodies whose physical properties differ so little as those of the hydrides and iso-hydrides under consideration, probably a larger proportion of the lesser constituent of the mixture may be present without affecting the boiling-point of the larger one, than was shown in the experiments of Berthelot and Alluard; and, in such a case, it may be found impossible to purify a body sufficiently for some of the requirements of an investigation. But the fact that the constituents of such a mixture may be brought into such proportions by fractional condensation as to give the true boiling-point of the larger constituent, must nevertheless be regarded as of great importance in many cases, since the boiling-point is frequently an invaluable means of controlling the formulæ in homologous series; and especially so when the body under examination contains so large an admixture of foreign substance that the vapor density and ultimate analysis cannot be relied upon, which might often occur. Evidently these are considerations to be taken into account in passing judgment upon the value of results of an investigation of a mixture of liquids based on a proximate analysis by any method of fractional distillation; and it cannot be too strongly maintained, that constancy of boiling-point, even if considered only as an approximative indication of the degree of purity, should nevertheless be regarded as of the highest importance, and scarcely less so that the separations should be made under the most favorable conditions for the removal of the largest possible amount of impurity,—conditions which certainly cannot be claimed for the old process of fractional distillation.

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* I propose to make a series of experiments on mixtures of pure liquid substances in definite proportions, with the view to determine whether, or to what extent, the observations of Berthelot and Alluard will hold true when a mixture, of constant boiling-point, and inseparable by the old method, is distilled through my regulated condenser; and at the same time to determine also, approximately, the degree of purity attainable by my method, as a test of the capability of the process.

2. AMYL HYDRIDE = C_5H_{12}.

Specific gravity 0.6400 at 0°; 0.6275 at 14°.2; 0.6269 at 15°; 0.6249 at 17°.*

Determination of Boiling-point.— The method employed in this, and in all of the determinations of boiling-points given in this paper, unless some variation is specially mentioned, was precisely the same as that described in detail in the memoir first above referred to, page 159, and following. As constancy of boiling-point and accuracy of determination of the same are of so much importance in this investigation, and as I have deviated in some respects from the usual method of taking boiling-points, attention is specially called to what is said in that memoir on this subject; more particularly to the remarks on the question as to whether the experiment should be conducted with the bulb of the thermometer in the liquid or in the vapor. Some experiments there recorded bearing on this question are also referred to.

In order to show more fully the degree of purity of the substances, and the degree of thoroughness and accuracy of the analysis of the petroleum which this may indicate, I shall give in each case the readings of the thermometer at stated intervals during the distillation either of the whole, or very nearly the whole, of the liquid employed in the experiment, taking a fair average of these as the observed boiling-point. This, it will be observed, is a much severer test of purity, and is attended with less liability to personal error, than the more common practice of simply noting the temperature at which a certain *degree* of constancy of boiling-point is observed, omitting to indicate the limits of the distilling temperature. The custom here referred to has the additional objection, moreover, that it is liable to convey a wrong impression as to the actual degree of purity of the liquid,— not giving sufficient data to enable others to judge of this and of the accuracy of the determination, — so desirable when dealing with mixtures, like those of the hydrocarbons from petroleum, that cannot be made to yield, by the common process, liquids having a constant boiling-point, nor, properly considered, a very near approach to one, but only a pretty long "boiling-space."

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* It being too generally the custom, as I have remarked on a former occasion, to determine the specific gravities of volatile liquids at the temperature most convenient at the time of the experiment, without regard to uniformity of practice, which is so highly desirable, I have been obliged, in order to make a satisfactory comparison of other determinations with my own, to repeat the determinations at the temperatures employed by the different observers. As the results of these determinations occupy so little space, I am induced to insert them, as they were all taken with great care, and by means of a specific gravity bottle of the best construction for volatile liquids. A description of this bottle is given in Vol. IX. (N. S.) p. 144, of the Memoirs of this Academy.

In the present experiment the readings of the thermometer were as follows: —

Observed temperature	of the liquid	at commencement of distillation,	29°.5
"	"	8 minutes later,	29°.7
"	"	10 "	29°.9
"	"	21 "	30°.1
"	"	5 "	30°.3

At the latter temperature the liquid had distilled almost to dryness; and at 31°, six minutes later, not a drop of liquid remained in the retort. The duration of the experiment was 50 minutes, and the range of distilling temperature 1°.5, or 0°.8, if we omit the last, and doubtless least reliable, observation. As the thermometer was doubtless directly influenced by the superheated retort-bottom during the distillation of the last few drops of liquid, the last observation is considered of no value except as furnishing additional evidence of the high degree of purity of the substance, i. e. for so volatile a body of this class, obtained by fractional distillation. That it should be otherwise disregarded is shown by the fact that the bulk of the liquid passed over with so slight a variation of temperature, viz. only 0°.4, from 29°.7 to 30°.1, during the long interval of 31 minutes. The average of the first five observations, or 29°.9, is therefore taken as the observed boiling-point; which, corrected for pressure and the upper mercurial column, becomes 30°.1, being almost identical with the boiling-point that Frankland originally found for this body. The latter circumstance, with other corroborative evidence, such as the fact that my analyses gave almost invariably a somewhat larger percentage of hydrogen for the members of my 1st series than for the corresponding terms of the 2d (which may prove, however, merely accidental), has led me, while somewhat in doubt on this point, to regard this body and its homologues of the 1st series as the true hydrides of the alcohol radicals, or marsh-gas series; and the 2d series, provisionally, as the iso-hydrides of these radicals, — a term which may be appropriately retained if further examination shall furnish no stronger evidence of difference in constitution. This view is strengthened further by the fact that other observers besides Frankland and myself have found the boiling-point of hydride of amyl 30°, or thereabouts; or that it would *begin* to boil at very nearly this temperature, indicating at least the probability that it *has not a higher* boiling-point, for the gaseous butyl hydride, the next lower body of the series, would probably have been so completely expelled from the liquid during the long-continued process of fractionation that the little which might remain would not sensibly lower the boiling-point of the amyl hydride. C. G. Williams * found that amyl hydride from Boghead naphtha boiled between 30° and 40°; and a preparation of the same from similar material from cannel coal gave Schorlemmer † the boiling-point 39°–40°; but subsequently he found that a preparation from American petroleum boiled at 34°,—which comes nearer to Williams's first observation than to the lower of his own previous observations; and since he states that he obtained a larger quantity of this, which would enable him to continue longer the process of fractionation, and since a preparation from this petroleum would doubtless contain less of contaminating substances that might influence the determination, it may be inferred that his later determination is probably the more reliable of the two. But Pelouze and Cahours ‡ make the boiling-point of this body from American petroleum exactly 30°, agreeing precisely with my own determination and with that of Dr. Frankland. Furthermore, Wurtz § states that amyl hydride from amyl alcohol boils also at 30°.

The determinations above quoted having been made previously to the publication of my petroleum series, probably neither of the investigators, either of the coal or petroleum naphtha, had the remotest idea of the presence of a series isomeric with the hydrides, and therefore made no special effort to sĕparate them; ‖ and since these determinations were evidently made on mixtures containing variable proportions, and in some cases a preponderating quantity, of these isomeric bodies, the disagreement between their results does not seem surprising, nor that the boiling-point should have been placed so high as 39°, or about that of the iso-hydride itself. In the absence of evidence, therefore, that the body described by Frankland boiling at 30° is *not* of the series of hydrides, it seems reasonable to take this, the one first described and best studied, as typical of this series; and to consider, for the present, those bodies that correspond with this in regard to their boiling-points and other properties, viz. those boiling at 0°, 60°, 90°, and 120°, respectively, as also of the same series; and those boiling at 9°, 39°, 69°, and 129°, as a series of isomers, or iso-hydrides; for it is well known with regard to the best-studied of homologous series of liquid bodies that, as a rule, a common boiling-point difference between the contiguous members prevails throughout any given series; any deviation from this being so exceptional as to justify a suspicion of error.* Nevertheless, the series of hydrides is generally represented with some of the boiling-points of one series and some of the other, while others do not agree with the true boiling-points of either series. It is hoped that the results recorded in this paper may serve to bring order out of this confusion.

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* Quarterly Journal of the Chemical Society, XV. 130.

† Journal of the Chemical Society, 1862, XV. 419.

‡ Bulletin de la Société Chimique, 1863, p. 231.

§ Comptes Rendus, 1862, LIV. 387.

‖ A re-examination by Schorlemmer has since confirmed my discovery of this series. Proceedings of the Royal Society, XIV. 468; Annalen der Chemie, CXXXV 269.

Analysis.†

0.1935 grm. of the substance gave 0.5912 of carbonic acid, and 0.2866 of water.

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* Note Goldstein's late paper.

† The analyses given in this paper having been made, for the most part, previously to the working out of my process for combustion in oxygen gas, above referred to, it is to be understood, unless otherwise stated, that they were made, so far as relates to those boiling under 150°, by distilling the vapor of the substance into a column of ignited oxide of copper, and completing the combustion in a stream of oxygen. This method, however, was not at first successful. So long as I continued to follow the direction of Regnault to connect the bulb with the combustion tube by means of a caoutchouc tube, I was unable to avoid a loss of several per cent, occasioned, doubtless, by the escape of substance through the material of the connecting tube. That this was the probable source of error was shown by suspending a piece of this tubing in the vapor of petroleum naphtha at the common temperature, the walls of the tube soon acquiring two or three times their original thickness, from absorption of hydrocarbon vapor. During an analysis, however, no change in the appearance of the tubing was noticed, — any perceptible thickening being prevented by the heat and exposure to air carrying away the vapor as fast as absorbed. To get over this difficulty, I contrived a convenient method of making the connection with the combustion tube by means of a cork. A tube, 4 or 5 inches or more in length, with a small bulb blown in the centre, and with capillary ends, was substituted for the ordinary bulb. By leaving the tube of sufficient length on each side of the bulb, the same bulb could be repeatedly used, only requiring

		Calculated.		Found.
Carbon	€_5	60	83.334	83.326
Hydrogen	H_{12}	12	16.666	16.448
			100.000	99.774

Determination of Vapor Density.

Temperature of balance	9°
Height of barometer	761.86 mm. at 0°
Temperature of oil bath	128°
Increment of balloon	0.2776
Capacity of balloon	235.5 c.c.
Density of vapor found	2.7642
Theory $\text{€}_5H_{12} = 4$ vols.	2.4932 *

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that the capillary ends should be drawn out anew for each analysis. This bulbous tube containing the liquid to be analysed was used in the following manner. A cork fitting the combustion tube was perforated to fit one end of the bulbous tube, and the latter tightly inserted in the perforation so that the whole of the long capillary end projected beyond the cork. This end of the bulbous tube was then introduced into the combustion tube, and the cork firmly pressed into its place. The cork being a suitably flexible one, the end of the capillary tube, at the proper moment, was readily broken off against the inner surface of the combustion tube, simply by a lateral pressure against the outer half of the cork.

The distillation of the material from the bulb was better controlled by means of a heated copper bar, as described in my paper "On a Process of Organic Elementary Analysis," etc., already referred to. When no longer a trace of liquid remained in the bulbous tube, connection with the oxygen gasometer was readily made by means of a caoutchouc tube, and communication established by breaking off the capillary end within the caoutchouc connecting tube by means of pliers against the sides of the tube. Before the latter was done, however, the oxygen was turned on, in order to produce pressure from behind, and thereby prevent a possible loss from passage of vapor backward.

When making several analyses in succession, the posterior end of the combustion tube was generally found too hot at the close of an analysis to admit of being so tightly clenched with the hand as is necessary in attaching the bulbous tube; and attempts to make a good connection in this manner under such circumstances were generally unsuccessful. To overcome this difficulty, I procured an iron clamp lined with cork, the lower half of which was attached with screws to the top of the combustion furnace in such a position that the combustion tube, at a convenient point near the end, would rest on the cork in the lower half of the clamp. The upper half of the clamp being then laid on and tightly screwed down, served to hold the tube so firmly that the whole force of the hand could be applied to the cork, and thus insure a perfectly tight joint without producing the slightest disturbance of the rest of the apparatus.

* $C = 0.831$; $H = 0.0693$. [Mem.] "Repeat this determination by my process."

3. AMYL ISO-HYDRIDE = C_5H_{12}.

Specific gravity 0.6454 at 0°; 0.6326 at 15°; 0.6306 at 17°

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	36°.6
Observed temperature of the liquid 38 minutes later	36°.6
" " " 20 " "	36°.7
" " " 10 " "	36°.7

Eight minutes later the liquid had all vaporized. The corrected boiling-point was found to be 37°.

Analysis.—By combustion with cupric oxide in the manner described under Hydride of Amyl, 0.1666 grm. of the substance gave 0.5068 of carbonic acid, and 0.2482 of water.

			Calculated.	Found.
Carbon	$Ȼ_5$	60	83.334	82.965
Hydrogen	H_{12}	12	16.666	16.555
			100.000	99.520

Determination of Vapor Density.

Temperature of balance	8°.5
Temperature of oil bath	129°
Height of barometer	778.8mm. at 0°
Increment of balloon	0.2255
Capacity of balloon	227.5 c.c.
Density of vapor found	2.514
Theory $Ȼ_5H_{12}$ = 4 vols.	2.4932

4. HEXYL HYDRIDE = C_6H_{14}.

Specific gravity 0.6762 at 0°; 0.6638 at 15°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	61°.0
Observed temperature of the liquid 1 minute later	61°.2
" " " 36 minutes "	61°.2

Five mintes later it had distilled to dryness. The temperature of the boiling liquid was, therefore, absolutely constant at 61°.2

during the space of thirty-six minutes. Its corrected boiling-point is 61°27.

Analysis 1.— 0.1808 grm. of the substance gave 0.5561 of carbonic acid, and 0.2698 of water.

		Calculated		Found.
Carbon	$€_6$	72	83.72	83.884
Hydrogen	H_{14}	14	16.28	16.580
			100.00	100.464

Analysis 2.— 0.226 grm. of the substance gave 0.6968 of carbonic acid, and 0.3291 of water.

Carbon	84.089
Hydrogen	16.181
	100.270

Determination of Vapor Density.

Temperature of balance	17°
Temperature of oil bath	121°
Height of barometer	764 mm. at 10°
Increment of balloon	0.3666
Capacity of balloon	238 c.c.
Vapor density found	3.0528
Theory $€_6H_{14}$ = 4 vols.	2.9735

5. HEXYL ISO-HYDRIDE = C_6H_{14}.

Specific gravity 0.689 at 0°; 0.6772 at 15°.

Determination of Boiling-point. — Conducting this experiment precisely as the preceding, the observed temperature of the liquid at the commencement of distillation was 68°.1, and it remained absolutely constant during the long space of 52 minutes, distilling down to a very small residue, which was left in the retort at this temperature. The corrected boiling-point was found to be 68°.5.

Analysis 1.— 0.1363 grm. of the substance gave 0.4214 of carbonic acid, and 0.194 of water.

		Calculated.		Found.
Carbon	$€_6$	72	83.72	84.43
Hydrogen	H_{14}	14	16.28	15.81
			100.00	100.24

Analysis 2.— 0.1700 grm. of the substance gave 0.5256 of carbonic acid, and 0.2412 of water.

			Calculated.	Found.
Carbon	Є_6	72	83.72	84.321
Hydrogen	H_{14}	14	16.28	15.765
			100.00	100.086

Determination of Vapor Density.

Temperature of balance	16°
Temperature of oil bath	129°
Height of barometer	762 mm. at 8°
Increment of balloon	0.8829
Capacity of balloon	262 c.c.
Density of vapor found	3.038
Theory $\text{Є}_6H_{14} = 4$ vols.	2.9737

6. Heptyl Hydride = C_7H_{16}.

Specific gravity 0.7183 at 0°; 0.7065 at 15°.
Specific gravity after treatment with nitric acid 0.7033.

Determination of Boiling-point.

Observed temperature at commencement of distillation	88°.7
" " 10 minutes later	88°.9
" " 17 " "	89°
" " 13 " "	89°.1
" " 5 " "	89°.3
" " 10 " "	89°.7

having distilled quite to dryness. Applying the usual corrections to the number 89°, the corrected boiling-point is found to be 90°.4. After treatment of a portion of this body with nitric acid, its corrected boiling-point was 90°.53. This experiment was made, however, on a very small quantity of liquid, and would hardly justify the conclusion that the acid had really effected a change of the boiling-point.

Analysis 1.— 0.2268 grm. of the substance gave 0.7031 of carbonic acid, and 0.3165 of water.

			Calculated.	Found.
Carbon	Є_7	84	84.00	84.55
Hydrogen	H_{16}	16	16.00	15.51
			100.00	100.06

Analysis 2. — 0.2187 grm. of the substance gave 0.6766 of carbonic acid, and 0.3064 of water.

		Calculated.		Found.
Carbon	$Є_7$	84	84.00	84.38
Hydrogen	H_{16}	16	16.00	15.57
			100.00	99.95

Determination of Vapor Density.

Temperature of balance	12°.5
Temperature of oil bath	134°
Height of barometer	746 mm. at 6°
Increment of balloon	0.4383
Capacity of balloon	242 c.c.
Density of vapor found	3.547
Theory $Є_7H_{16}$ = 4 vols.	3.458

7. HEPTYL ISO-HYDRIDE = C_7H_{16}.

Specific gravity 0.7299 at 0°; 0.7184 at 15°. After treatment with an excess of monohydrated nitric acid, specific gravity 0.7048 at 16°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation	96°.6
Observed temperature of the liquid 10 minutes later	96°.8
" " " 15 " "	96°.9
" " " 20 " "	97°.2

Having had occasion to leave the experiment for a few moments at this juncture, on returning ten minutes later it was found that the liquid had distilled to dryness. The average of the observations 96°.8 and 97°.2 is 97°. Applying the proper corrections, we find the corrected boiling-point to be 98°.1.

After treatment of a small portion of this oil with monohydrated nitric acid, its corrected boiling-point was then 97°.85; but, as in the last experiment, the quantity of oil operated upon was too small to admit of making a very exact determination.

Analysis. — 0.2073 grm. of the substance gave 0.6469 of carbonic acid, and 0.2862 of water.

		Calculated.		Found.
Carbon	Ꞓ_7	84	84.00	85.11
Hydrogen	H_{16}	16	16.00	15.34
			100.00	100.45

Determination of Vapor Density.

Temperature of balance	17°
Temperature of oil bath	138°.5
Height of barometer	763.4 mm. at 9°
Increment of balloon	0.4236
Capacity of balloon	228.5 c.c.
Density of vapor found	3.546
Theory Ꞓ_7H_{16} = 4 vols.	3.389

8. Octyl Hydride = C_8H_{18}.

Specific gravity 0.7374 at 0°; 0.7262 at 15°.

Determination of Boiling-point. — The quantity of liquid at my disposal for this experiment was considerably smaller than that employed in the determinations above detailed; therefore, instead of using a retort, the distillation was made from a large, long-necked bulb. Since in this case the whole of the mercury was situated below the cork, and surrounded by the hot ascending vapors, no correction for the mercurial column is required.

Observed temperature of the liquid at commencement of distillation						119°.1
Observed	temperature	of the liquid	5	minutes	later	119°.2
"	"	"	10	"	"	119°.4
"	"	"	2	"	"	119°.6
"	"	"	3	"	"	120°

At the latter point it had distilled nearly to dryness. This determination was made under normal atmospheric pressure, and therefore requires no correction. Taking the average of the five observations, we find the boiling-point to be 119°.5.

Analysis.[*]

Determination of Vapor Density.

Temperature of balance	12°
Temperature of oil bath	198°
Height of barometer	777 mm. at 9°
Increment of balloon	0.3889
Capacity of balloon	215.5 c.c.
Density of vapor found	3.992
Theory $\text{Ꞓ}_8\text{H}_{18}$ = 4 vols.	3.9425

9. OCTYL ISO-HYDRIDE = C_8H_{18}.

Specific gravity 0.7516 at 0°; 0.7430 at 15°.

Determination of Boiling-point. — This experiment was conducted in the manner described under octyl hydride, and for the same reason there stated. Atmospheric pressure normal.

Observed temperature of the liquid at commencement of distillation	126°.8
Observed temperature of the liquid 10 minutes later	127°.0
“ “ “ 5 “ “	127°.2
“ “ “ 4 “ “	127°.4
“ “ “ 6 “ “	129°.1

Average boiling-point 127°.6.

Analysis.[†]

Determination of Vapor Density.

Temperature of balance	13°
Temperature of oil bath	211°
Height of barometer	777 mm. at 9°
Increment of balloon	0.3662
Capacity of balloon	212 c.c.
Density of vapor found	3.9900
Theory $\text{Ꞓ}_8\text{H}_{18}$ = 4 vols.	3.9425

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[*] A memorandum written by the author in pencil on the margin of his MS. reads, after the word Analysis, “Not made, August, 1868.”

[†] A note by the author reads: “Analysis not yet made, August, 1868.” Another memorandum reads: “Storer and W. [in their memoir on the Exam-

10. Nonyl Hydride = C_9H_{20}.

Specific gravity 0.7555 at 0°; 0.7447 at 15°.

Determination of Boiling-point.

Observed temperature of the liquid at commencement of distillation					148°.7
Observed temperature of the liquid			15	minutes later	148°.7
"	"	"	15	" "	148°.9
"	"	"	5	" "	149°.1
"	"	"	13	" "	149°.4
"	"	"	2	" "	149°.7

Average of observations 149°.2. Corrected boiling-point 150°.6. Average of two determinations 150°.8.

Analysis.— 0.1841 grm. of the substance gave 0.5765 of carbonic acid, and 0.2526 of water.

		Calculated.		Found.
Carbon	$Ꞓ_9$	108	84.375	85.40
Hydrogen	H_{20}	20	15.625	15.24
			100.000	100.64

Determination of Vapor Density.

Temperature of balance	18°.5
Temperature of oil bath	220°
Height of barometer	756.3 mm. at 17°
Increment of balloon	0.4649
Capacity of balloon	234 c.c.
Density of vapor found	4.460
Theory $Ꞓ_9H_{20}$ = 4 vols.	4.426

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ination of a Hydrocarbon Naphtha, obtained from the products of the Destructive Distillation of Lime-soap, Memoirs of the American Academy, 1865 (N. S.), IX. 177] say H[ydride] of C[apryl] boils at 128°, near bottom of page 195, and elsewhere? [i. e. page 194]. Perhaps I should call the '8 bodies' [viz. those boiling at 8°, 38°, and so on] hydrides, and the '10 bodies' [boiling at 0°, 30°, etc.] iso-hydrides? See Schorlemmer's late work, and compare with Wurtz's bodies from amyl alcohol." It appears, however, that this hesitancy was but momentary, for, as is to be seen above, on pages 70, 71, he finally accepted Frankland's hydride of amyl, boiling at 30°, as the prototype of the normal hydrides, and relegated the substance boiling at 128° to the second series, of which it is the last term. Note by F. H. Storer.

$Ꞓ_nH_{2n}$ Series.

1 Rutylene = $C_{10}H_{20}$.

Specific gravity 0.7703 at 0°; 0.7598 at 15°.

1. *Determination of Boiling-point.*—By the thermometer employed, water was found to boil at 101°.1.

Observed temperature of liquid at commencement of distillation	172°.5
Observed temperature of liquid 7 minutes later	172°.7
“ “ “ 8 “ “	173°
“ “ “ 5 “ “	173°.3
“ “ “ 5 “ “	173°.7
“ “ “ 2 “ “	174°

Had distilled nearly to dryness. Taking the average of the six observations, and applying the proper corrections for pressure and the upper mercurial column, and also deducting 1°.1 for the error of the thermometer, the corrected boiling-point is found to be 174°.9.

2. *Determination of Boiling-point.* — By the thermometer employed water boiled at 100°.5. This experiment was conducted precisely as the last, and the material employed was the same.

Observed temperature of liquid at beginning of distillation	172°.3
Observed temperature of liquid 5 minutes later	172°.5
“ “ “ 13 “ “	172°.8
“ “ “ 22 “ “	173°
“ “ “ 10 “ “	172°.9
“ “ “ 10 “ “	172°.9
“ “ “ 5 “ “	173°

Five minutes later had distilled nearly to dryness, the temperature having risen to 173°.8. Taking 173° as the observed boiling-point, and making the proper corrections for pressure and the mercurial column, and also deducting the error of the thermometer, 0°.5, gives 175°.3 as the corrected boiling-point.

Analysis 1. — 0.1257 grm. of the substance gave 0.3951 of carbonic acid, and 0.1713 of water.

		Calculated.		Found.
Carbon	$Ꞓ_{10}$	120	85.71	85.720
Hydrogen	H_{20}	20	14.29	15.139
			100.00	100.859

Analysis 2. — 0.2689 grm. of the substance gave 0.8398 of carbonic acid, and 0.3577 of water.

		Calculated.		Found.
Carbon	$Ꞓ_{10}$	120	85.71	85.18
Hydrogen	H_{20}	20	14.29	14.78
			100.00	99.96

Determination of Vapor Density.

Temperature of balance	18°
Temperature of oil bath	236°
Height of barometer	757.4 mm. at 17°
Increment of balloon	0.5743
Capacity of balloon	249 c.c.
Density of vapor found	5.066
Theory $Ꞓ_{10}H_{20}$ = 4 vols.	4.843

2. MARGARYLENE = $C_{11}H_{22}$.

Specific gravity, 0.7822 at 0°; 0.7721 at 15°.

Determination of Boiling-point.

Observed temperature of liquid at commencement of distillation	192°.5
Observed temperature of liquid 3 minutes later	192°.7
" " " 5 " "	193°.
" " " 10 " "	193°.5

Five minutes later the bottom of the retort had become nearly dry, the temperature having reached 194°.5. The average of the first four observations is 193°; and the corrected boiling-point 195°.4. A second determination, by another thermometer, gave the corrected boiling-point 196°.2; the average of the two determinations being 195°.8.

Analysis 1. — 0.197 grm. of the substance gave 0.6183 of carbonic acid, and 0.2624 of water.

		Calculated.		Found.
Carbon	$Ꞓ_{11}$	132	85.71	85.60
Hydrogen	H_{22}	22	14.29	14.80
			100.00	100.40

Analysis 2. — 0.1997 grm. of the substance gave 0.6248 of carbonic acid, and 0.2633 of water.

		Calculated.		Found.
Carbon	$Ꞓ_{11}$	132	85.71	85.33
Hydrogen	H_{22}	22	14.29	14.65
			100.00	99.98

Determination of Vapor Density.

Temperature of balance	14°.5
Temperature of oil bath	250°
Height of barometer	767 mm. at 13°
Increment of balloon	0.6227
Capacity of balloon	247.5 c.c.
Density of vapor found	5.480
Theory $Ꞓ_{11}H_{22}$ = 4 vols.	5.327

3. LAURYLENE = $C_{12}H_{24}$.

Specific gravity 0.7905 at 0°; 0.7804 at 15°.

1. *Determination of Boiling-point.* — By the thermometer employed, water boiled at 100°.5.

Observed temperature of the liquid at commencement of distillation	212°
Observed temperature of the liquid 16 minutes later	212°.3
" " " 9 " "	212°.7
" " " 4 " "	213°

Three minutes later the boiling-temperature was 214°, having distilled nearly to dryness. The average of the first five observations is 212°.5. Deducting the error of the thermometer, 0°.5, and making the usual corrections for pressure and the upper column of mercury, the corrected boiling-point is found to be 216°.8.

2. *Determination of Boiling-point.* — The conditions of this experiment were the same as the last, with the exception that by the thermometer employed, water boiled at 101°.1.

Observed temperature of the liquid at beginning of distillation						210°.3
Observed temperature of the liquid			5	minutes	later	210°.7
"	"	"	3	"	"	211°
"	"	"	5	"	"	211°.5
"	"	"	4	"	"	212°

Had distilled nearly to dryness at 212°5. Average of the six observations, 211°; corrected boiling-point, 215°.5. Average of both determinations, 216°.2.

Analysis 1. — 0.1401 grm. of the substance gave 0.4349 of carbonic acid, and 0.1872 of water.

		Calculated.		Found
Carbon	$Ȼ_{12}$	144	85.71	84.66
Hydrogen	H_{24}	24	14.29	14.85
			100.00	99.51

Analysis 2. — 0.1934 grm. of the substance gave 0.608 of carbonic acid, and 0.2551 of water.

		Calculated.		Found.
Carbon	$Ȼ_{12}$	144	85.71	85.74
Hydrogen	H_{24}	24	14.29	14.66
			100.00	100.40

Determination of Vapor Density.

Temperature of balance	12°.5
Temperature of oil bath	274°
Height of barometer	762.6 mm. at 4°
Increment of balloon	0.6905
Capacity of balloon	253 c.c.

Density of vapor found	6.090
Theory, $Ȼ_{12}H_{24}$ = 4 vols.	5.812

Having already given tables of the boiling-points, — the determinations of which are above detailed, — with such deductions and remarks as seemed appropriate, I will now proceed to treat the other results in a similar manner. A comparison of these results, which the tables will greatly facilitate, will bring to view some interesting relations.

TABLE I. — *Showing the Difference of Specific Gravity corresponding to Difference of Boiling-point of the Bodies obtained from Pennsylvania Petroleum, arranged in the Order of the Boiling-points, regardless of Serial Classification or Elementary Difference; and also showing the Differences of Specific Gravity at* 0° *and* 15°.

Name.	Formula.	Boiling-point.	Specific Gravity at 0°.	Difference of Boiling-point.	Difference of Specific Gravity.	Specific Gravity at 15°.	Difference of Sp. Gr. at 0° and 15°
Butyl Hydride	C_4H_{10}	° 0.0*	0.6000*	° —	—	—	—
" Isohydride	"	8–9	0.6107	8.5	0.0107	0.5967†	0.0104†
Amyl Hydride	C_5H_{12}	30.2	0.6400	21.3	0.0293	0.6269	0.0131
" Isohydride	"	37.0	0.6454	6.8	0.0054	0.6326	0.0128
Hexyl Hydride	C_6H_{14}	61.3	0.6762	24.3	0.0308	0.6638	0.0124
" Isohydride	"	68.5	0.6893	7.2	0.0131	0.6772	0.0121
Heptyl Hydride	C_7H_{16}	90.4	0.7183	21.9	0.0290	0.7065	0.0118
" Isohydride	"	98.1	0.7299	7.7	0.0116	0.7184	0.0115
Octyl Hydride	C_8H_{13}	119.5	0.7374	21.4	0.0075	0.7262	0.0112
" Isohydride	"	127.6	0.7516	8.1	0.0142	0.7430	0.0086
Nonyl Hydride	C_9H_{20}	150.8	0.7555	23.2	0.0039	0.7447	0.0108
Rutylene	$C_{10}H_{20}$	174.9	0.7703	24.1	0.0148	0.7598	0.0105
Margarylene	$C_{11}H_{22}$	195.8	0.7822	20.9	0.0119	0.7721	0.0101
Laurylene	$C_{12}H_{24}$	216.2	0.7905	20.4	0.0083	0.7804	0.0101

Average difference of boiling-point between the corresponding hydrides and isohydrides 7°.7 nearly.

* Ronald's determination. † Calculated.

TABLE II. — *Showing the Difference of Specific Gravity at* 0° *corresponding to the Common Difference of about* 30° *between their Boiling-points, and to the Elementary Difference of* CH_2 *in the Series of Hydrides.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Butyl Hydride	C_4H_{10}	0.0*	0.6000*	—	—	—
Amyl “	C_5H_{12}	30.2	0.6400	CH_2	30.2	0.0400
Hexyl “	C_6H_{14}	61.3	0.6762	CH_2	31.1	0.0362
Heptyl “	C_7H_{16}	90.4	0.7183	CH_2	29.1	0.0421
Octyl “	C_8H_{18}	119.5	0.7374	CH_2	29.1	0.0191
Nonyl “	C_9H_{20}	150.8	0.7555	CH_2	31.3	0.0181

Average difference of boiling-point 30°.16.
“ “ specific gravity 0.0311.
“ “ “ “ below 100° of boiling-point, 0.0394;
and above 100°, 0.0186.

TABLE III. — *Showing the Difference of Specific Gravity at* 0° *corresponding to the Common Difference of about* 30° *between their Boiling-points, and to the Elementary Difference of* CH_2 *in the Series of Isohydrides.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Butyl Isohydride	C_4H_{10}	8–9	0.6107	—	—	—
Amyl “	C_5H_{12}	37.0	0.6454	CH_2	29.5	0.0347
Hexyl “	C_6H_{14}	68.5	0.6893	CH_2	31.5	0.0439
Heptyl “	C_7H_{16}	98.1	0.7299	CH_2	29.6	0.0406
Octyl “	C_8H_{18}	127.6	0.7516	CH_2	29.5	0.0217

Average difference of boiling-point, 30°.03.
“ “ specific gravity, 0.0352.
“ “ “ “ below 100° of boiling-point, 0.0397.
Difference of specific gravity above 180° of boiling-point, 0.0217.

* Ronald's determination.

TABLE IV. — *Showing the Difference of Specific Gravity at 0° corresponding to the Common Difference of about 20° between the Boiling-points, and to the Elementary Difference of CH_2 in the C_nH_{2n} Series.*

Name.	Formula.	Boiling-point.	Specific Gravity.	Elementary Difference.	Difference of Boiling-point.	Difference of Specific Gravity.
Rutylene	$C_{10}H_{20}$	174.9	0.7703	—	—	—
Margarylene	$C_{11}H_{22}$	195.8	0.7822	CH_2	20.9	0.0119
Laurylene	$C_{12}H_{24}$	216.2	0.7905	CH_2	20.4	0.0083

NOTE ON A MEMOIR BY C. SCHORLEMMER.

There was found among Warren's papers, in the same portfolio with the manuscript of the foregoing memoir, a printed copy of a memoir "On the Normal Paraffins" (taken from the Philosophical Transactions, 1872, Vol. CLXXII.), which had been presented to Warren by its author, Dr. Schorlemmer. Upon the last page of this presentation copy Warren had written in pencil some memoranda which, under the peculiar circumstances of the case, seem to be worthy of being put upon record.

For the sake of clearness, page 123 of Schorlemmer's memoir is here copied, in quotation marks, together with the memoranda which stand written upon that page of the memoir in Warren's handwriting.

It is to be observed that both the side-note, at the left of the tabular matter, as printed on the next page, and the column of figures headed "Difference found," at the right of the table, were written by Warren. The asterisk also, affixed to the word "Butane" in the table, and the foot-note to which this asterisk refers, are copied from Warren's memoranda.

Homologues of Marsh Gas.

			" Boiling-points. Mean found.	Calculated.	Difference."	Difference found.	
	" CH_4	Methane					
	C_2H_6	Ethane					
	C_3H_8	Propane					
	C_4H_{10}	Butane *	1°	1°			
37° to 39°, p. 114	C_5H_{12}	Pentane	38	38	37	37	
600 c.c. 97°.5 to 98°. Remainder 98° to 99°, p 121	C_6H_{14}	Hexane	70	71	33 = 37—4	32	37 − 2 = 5
	C_7H_{16}	Heptane	99	100	29 = 33—4	29	
	C_8H_{18}	Octane	124	125	25 = 29—4	25	
	$C_{12}H_{26}$	Dodecane	202	201	4 × 19		
	$C_{16}H_{34}$	Hecdecane	278	278	4 × 19 "		

"In calculating the boiling-points, it was assumed, as appears to be the case, that the difference decreases regularly by 4 until it reaches the well known difference 19°."

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* This Butane, C_4H_{10}, corresponds to the first member of my first series, which I call the normal hydrides of the alcohol radicals, the series above given being isomeric with the hydrides.

According to my observations "Butane" should boil at about 8° to 9°, and its isomeride at 0° instead of 1°. Taking 8° to 9° as the boiling-point of Butane, the difference of boiling-point between it and "Pentane" would be 29° to 30°.

Taking 29° to 30° as the starting point for his calculated differences, and deducting 4° successively, we have

29° to 30° — 4° = 25° to 26° Pentane and Hexane.
25° to 26° — 4° = 21° to 22° Hexane and Heptane.
21° to 22° — 4° = 17° to 18° Heptane and Octane.

VII.

NOTE ON A CRITICISM OF THE AUTHOR'S APPARATUS FOR FRACTIONAL CONDENSATION.*

By C. M. Warren,

Professor of Organic Chemistry, Massachusetts Institute of Technology.

The supplement of the American edition of the Chemical News for February, 1869, contains an article on "Cracking of Petroleums," by the editor of the supplement, which closes with the following paragraph: —

"In conclusion, we offer the suggestion to those who analyze oils by fractional distillation that they take pains to avoid the conditions which favor cracking; by not observing such caution the analyses of petroleums hitherto made have generally been vitiated, in fact, very many have been worthless. Perhaps it is not possible to avoid all the error that may arise from cracking, yet it may easily be brought so low as to be insignificant. Of the apparatus which has been devised for fractional distillation probably the one least suitable for petroleums and other unstable liquids is that of Prof. C. M. Warren. Warren's still probably answers well enough for alcohols, essential oils, and the benzole series, but cracking can scarcely be avoided when it is used for petroleums."

I am induced to notice the above criticism from the fact, to which it recalls my attention, that the question of adaptability for the separation of bodies more or less liable to decomposition by heat in distillation, as compared with that of the common forms of distillatory apparatus, was not specially considered in my memoir descriptive of my process,† an omission which, it now appears, it might have been better not to have made. It was not, however, from oversight that this was omitted, but because it was thought that no one could fail to see, on a moment's reflection, that the conditions to which liquids are subjected in my apparatus, so far as these may be of a nature to affect the liability to decomposition, are quite the same as those attending fractional distillation by the common process. It was therefore deemed sufficient to make no further allusion to this matter than was done, indirectly, in recommending my process for the separation of "*bodies not decomposed by heat in distillation*" (p. 134 of the original memoir), clearly implying that I did not regard it as faultless for the opposite class of substances; and sufficient, it would seem, to put any one on his guard who would make such use of it. Nevertheless, as I hold that my process introduces no new condition favorable to decomposition, even of bodies liable to partial change of this nature during distillation, I do not hesitate to recommend it also as preferable to the old process for this very class of substances, — when distillation cannot be altogether avoided, — since the length of time required to effect an equal or better separation may thereby be very much shortened, and consequently the aggregate amount of decomposition materially and proportionately lessened. But in operating upon such substances it would be unadvisable to continue the process longer than absolutely necessary to obtain the best approximation to the desired result which the nature of the material would admit of; and the same is of course true of the old process.

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* It would appear that this article was written in 1869. Two manuscript copies of it were found among the author's papers after his death, viz. a rough draft, and a fair copy ready for the printer's hands. The latter is here printed, without change.

† Memoirs of the American Academy, 1864; American Journal of Science, 1865; Chemical News, 1865.

Not to enter into much detail, it may be stated that the only essential difference between my apparatus and that in common use for fractional distillation consists in the elevated condenser which I interpose between the retort and the ordinary condenser, discharging itself backward into the retort, its temperature being regulated by a separate flame, and maintained a few degrees (more or less, according to the nature or purity of the substance to be distilled) below the temperature of the retort.

In other forms of apparatus, there being no regulated condenser to effect a separation of the mixed vapors that escape from the retort, the whole of these go forward and are condensed together, the resulting liquid falling into the receiver.

Both in my process and in the common process the liquid in the retort is simply maintained in a state of ebullition under atmospheric pressure; consequently it is no more favorably conditioned for decomposition, in respect to temperature, in the one case than in the other.

The elevated condenser being kept at a lower temperature than that of the retort, it seems needless to say, has no effect to raise the temperature of the latter, but, on the contrary, holds it in check; and by proper management may serve to secure the conditions most favorable for taking off the largest possible quantity of the most volatile constituent at any time present, and this at the lowest possible temperature, not only of the vapor to be collected, but also of the liquid in the retort, — operating therefore advantageously, rather than unfavorably, with respect to decomposition. And yet I suspect, as he does not specify, that this is the identical feature of my process — being its chief or only distinctive feature — which has occasioned my critic's misconception with regard to the utility of the apparatus. It would evidently require a considerably longer time to distil a given quantity of a mixture of liquids of different boiling-points in my apparatus, if used as recommended for stable liquids, than in the common form, since in a single operation the larger part of the mixture is in reality many times condensed and re-distilled. Can this be his stumbling-block, — that he has not taken into consideration the relative amount of actual work (not measurable, however, by the *quantity* of liquid distilled, but by the *degree of purity* of the products obtained) that may be done with this apparatus in a given time as compared with the common apparatus?

If the liquid is not subjected to a higher temperature in the one apparatus than in the other, it is evident that superiority on the score of decomposition must be awarded to the one capable of giving the best results in the shortest space of time, since the amount of decomposition must be proportional to the time occupied. If objection is made to the repeated condensation and re-distillation that take place in my apparatus, I have only to say that this is a necessary condition of any effective process of fractional distillation; and if, to avoid cracking, this condition must be abandoned, and the vapors, as they rise laden with impurities, are immediately condensed in the receiver, then must fractional distillation itself be abandoned as a worthless process.

It has probably escaped my critic's scrutiny that my apparatus does not require to be employed in precisely the manner that I recommended for stable liquids; and a judicious chemist would modify the conditions to suit the nature of the material to be examined, — I refer to the adjustment of the temperature of the elevated condenser. In operating on perfectly stable liquids, I have found it advisable to keep the elevated condenser at as low a temperature as would permit the vapor of the most volatile liquid to pass through it; for in proportion as its temperature is higher than this, the product will contain a larger quantity of the less volatile constituents; and if the temperature be allowed to equal that of the retort, the conditions of the experiment would not differ essentially from ordinary distillation, except that friction, from contact of the vapor with the sides of the worm during its passage through the elevated condenser, might give it some slight advantage. Between these two extremes of temperature for the elevated condenser, therefore, it may be adjusted suitably for any unstable liquid requiring and admitting purification by distillation, since the time required to distil a given quantity of liquid by this process may be shortened, other things equal, in proportion as the temperature of the elevated condenser is raised nearer to that of the retort; and by shortening the time, other conditions the same, decomposition, as said before, is proportionately lessened.

I might give the details of many experiments to prove the superiority above claimed for my apparatus, for it has given me reliable results under the most varied conditions; but this does not seem to be required. I trust that the foregoing remarks will be sufficient to lead any one who may have questioned the adaptability of my apparatus for the class of substances now under discussion to view it in a different light.

VIII.

CONTRIBUTION FROM THE SALISBURY LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.

ON THE FORMATION OF THE ANHYDRIDES OF BENZOIC AND SUBSTITUTED BENZOIC ACIDS.

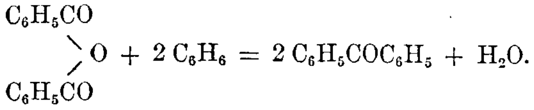
By George D. Moore and Daniel F. O'Regan.

Presented by Professor L P Kinnicutt, April 13, 1892.

By the action of phosphoric anhydride upon benzoic acid and an excess of benzol at 180–200°, Kollarits and Merz * obtained benzophenone. The course of the reaction is shown by the following equation:

$$C_6H_5COOH + C_6H_6 = C_6H_5COC_6H_5 + H_2O.$$

The same result was also obtained when, instead of benzoic acid, benzoic anhydride was employed:



$$\left.\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix}\right\rangle O + 2\,C_6H_6 = 2\,C_6H_5COC_6H_5 + H_2O.$$

In a second paper † on this subject, the same authors state that the formation of benzoic anhydride may possibly precede that of benzophenone, and add that, if such is the case, benzophenone must be formed by the direct action of benzoic anhydride upon benzol, even in absence of phosphorpentoxide. This last result they were unable to effect, even at temperatures ranging as high as 300°. Similar negative results were likewise obtained when toluol was employed instead of benzol. They therefore conclude that benzophenone is the product of the direct action of phosphorpentoxide upon benzoic acid and benzol.

The following experiments were undertaken with a view to studying more carefully the conditions of possible formation of

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* Zeitschr. für Chemie, 1871, p. 705. Berichte, V. 447.

† Berichte, VI. 537.

anhydrides as intermediary products in the synthesis of ketones from benzoic and substituted benzoic acids and hydrocarbons. If anhydrides are formed at all, it is reasonable to suppose that the reaction takes place at a temperature comparatively lower than that required for the ketone condensation; and we find that this is in fact the case.

I. *Action of Phosphorpentoxide upon Benzoic Acid in an Excess of Benzol.*

10 grams of benzoic acid, previously melted, pulverized, and thoroughly dried, were dissolved on the steam bath in about 200 c.c. of dry benzol, 10 grams phosphorpentoxide added to the hot solution, and the whole boiled under a reverse condenser for about four hours. The phosphorpentoxide did not appear to dissolve, but settled to the bottom of the flask in the form of an amorphous, gelatinous mass, which became gradually darker, until at the end of the operation, it was nearly black.

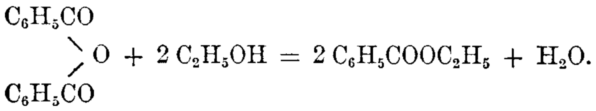
The supernatant benzol solution was of a light amber color. It was filtered hot from the insoluble residue, and, as no precipitate was deposited after standing over night, concentrated to about one third of its volume. On cooling, this solution threw down a copious precipitate of fine white needles, which were freed from the benzol mother-liquor by pressing between filter-paper, washed with dilute potash solution to remove possible traces of benzoic acid, and the residue taken up in ether. After one or two washings with water, the ether solution was drawn off, and the residue, after distilling off the ether, dissolved in ligroine. From this it crystallized in fine prismatic needles melting at 41–42°. On analysis the substance gave the following values: —

0.2153 grm. gave 0.5832 grm. CO_2 and 0.0903 grm. H_2O.

	Calculated for $\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\!>O.$	Found
C	74.33	73.87
H	4.43	4.60

The melting point and composition of the body show it to be without doubt benzoic anhydride, and the study of its properties confirms this conclusion. It consists of fine, prismatic, needle-like forms, easily soluble in alcohol, ether, benzol, chloroform and carbon disulphide, difficultly in water and in petroleum ether. This last is the best medium for its crystallization. Cold water converts it slowly, boiling water rapidly, into benzoic acid. Alkalies transform it into benzoic acid salts, from the solutions of which mineral acids precipitate benzoic acid in its characteristic leaflets.

The gelatinous phosphoric anhydride residue from the original benzol solution gave on extraction with benzol only a trace of anhydride. As this extract did not appear to contain any other substance, the gelatinous residue was taken up in absolute alcohol, with a view of thus isolating any benzophenone which might have been formed. As the alcohol was poured upon the residue, considerable heat was manifested. The alcoholic solution was concentrated to a small volume, but no crystals could be obtained. After some days, the alcohol having entirely disappeared, there remained in the beaker a small quantity of a pleasant-smelling, oily liquid. This was taken up in water to remove the phosphoric acid, washed with dilute potash to remove benzoic acid, and extracted with ether. Finally there remained a few drops of a brownish-colored oil, which, from its odor, we concluded was benzoic ethyl ester. Unfortunately the amount was too small and too impure to admit of analysis. Its formation may be ascribed to the following reaction: —



$$\left.\begin{matrix} C_6H_5CO \\ C_6H_5CO \end{matrix}\right> O + 2\,C_2H_5OH = 2\,C_6H_5COOC_2H_5 + H_2O.$$

It is probable that the anhydride necessary for this reaction was retained, mechanically enclosed, in the gelatinous phosphorous residue, from which it is but incompletely extracted by treatment with benzol. Phosphoric anhydride being readily soluble in alcohol, the formation of the ester is easily accounted for. In subsequent experiments we obtained some more of this oil, which boiled between 215° and 225°, (benzoic ethyl ester boils at 211–212°,) but could not get it in sufficiently large quantity to purify for analysis. The formation of esters of the nitrobenzoic acids, as described hereafter, under similar conditions, render it practically certain that the substance we have just described is benzoic ethyl ester.

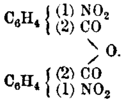
II. *Action of Phosphorpentoxide upon Orthonitrobenzoic Acid in an Excess of Benzol.*

10 grams *o*-nitrobenzoic acid, melting point 147°, were dissolved in about 200 c.c. of pure, dry benzol, 10 grams phosphorpentoxide

added to the hot solution, and the whole boiled on the steam bath for about three hours. As with benzoic acid, the phosphorpentoxide did not dissolve, but settled to the bottom of the flask as an amorphous, gelatinous mass, which became gradually darker-colored as the heating progressed, until, at the end of the operation, it was almost black. The amber-colored, supernatant liquid was decanted hot through a plaited filter and allowed to crystallize. After standing over night it had thrown down a considerable quantity of large, feather-shaped crystals, which, as their amount did not appear to increase on longer standing, were filtered, and washed with dry benzol. Their melting point, 147°, and ready solubility in alkalies, as well as their characteristic sweet taste, showed them to be the unchanged *o*-nitrobenzoic acid.

The mother-liquor from these crystals was concentrated to about one third of its original volume and allowed to stand. The result was a precipitate of short, thick, prismatic crystals, entirely different from the feather-shaped forms of the nitro acid, and melting at 128° to 130°. By repeated crystallization from benzol, this melting point was raised to 133°, at which temperature it remained constant. The analyses gave the following results: —

0.3393 grm. substance gave 25 c.c. nitrogen at 3.2° and 749.8 mm.
0.2564 grm. substance gave 0.5016 grm. CO_2 and 0.0700 grm. H_2O.

	Calculated for  $\begin{array}{l} C_6H_4\left\{\begin{array}{l}(1)\ NO_2\\ (2)\ CO\end{array}\right. \\ \qquad\qquad > O. \\ C_6H_4\left\{\begin{array}{l}(2)\ CO\\ (1)\ NO_2\end{array}\right. \end{array}$	Found.
C	53.16	53.34
H	2.53	3.03
N	8.86	8.96

In its properties the substance agrees with those assigned to the anhydride of orthonitrobenzoic acid by Bischoff and Roch,* viz. difficultly soluble in water and ether, more readily in alcohol, benzol, and glacial acetic acid. Heated quickly upon platinum foil it explodes. Continued treatment with boiling water or with alkalies converts it into the acid. Bischoff and Roch place the melting point of the anhydride at 135°, while we have not been able to raise it above 133°.

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* Berichte, XVII. 2789.

The phosphoric anhydride residue from which the benzol solution of *o*-nitro acid and anhydride had been decanted, yielded only a small amount of the acid on being extracted with fresh benzol. As a considerable quantity of insoluble residue still remained after repeating the operation, we substituted absolute alcohol for benzol as an extracting agent. With this we obtained a clear solution which was evaporated to dryness, washed with cold water until free of phosphorus, and recrystallized from alcohol. The product consisted of small tablets which melted at 30°, and is in all probability the ethyl ester of orthonitrobenzoic acid. The amount was too small for an analysis.

III. *Action of Phosphorpentoxide upon Meta Nitrobenzoic Acid in an Excess of Benzol.*

10 grams *m*-nitrobenzoic acid were dissolved in about 200 c.c. dry benzol, 10 grams of phosphorpentoxide added to the hot solution, and the whole boiled for three to four hours on the steam bath under a reverse condenser. As in the previous experiments, the phosphorpentoxide did not dissolve, but settled to the bottom of the flask as a thick, gummy mass, which, as the boiling continued, became rapidly darker-colored.

The supernatant liquid was decanted hot through a plaited filter, the residue in the flask boiled with fresh benzol, and this extract added to the first. The solution immediately threw down a precipitate of fine white needles, which, after drying, showed a melting point of 161°, which was not raised by recrystallization from benzol. Dried at 110° the substance analyzed as follows: —

0.3051 grm. gave 0.5871 grm. CO_2 and 0.0548 grm. H_2O.
0.2032 grm. gave 0.3904 grm. CO_2 and 0.0611 grm. H_2O.
0.2166 grm. gave 0.4160 grm. CO_2 and 0.0608 grm. H_2O.
0.3875 grm. gave 28.6 c.c. nitrogen at 6.6° and 748 mm.
0.4021 grm. gave 32.6 c.c. nitrogen at 4.2° and 755.7 mm.

	Calculated for $\left.\begin{array}{l}C_6H_4\left\{\begin{array}{l}(1)\ NO_2\\(3)\ CO\end{array}\right.\\C_6H_4\left\{\begin{array}{l}(3)\ CO\\(1)\ NO_3\end{array}\right.\end{array}\right\rangle O.$	Found. I.	 II.	 III.
C	53.16	52.48	52.40	52.37
H	2.53	2.00	3.34	3.14
N	8.86	8.82	8.70	

The complete combustion of the body is an exceedingly difficult operation. The substance must be thoroughly mixed with the oxide of copper or lead chromate, and burned very slowly in a generous current of oxygen. Even under these conditions the values for carbon are quite low. The chemical relations of the body, however, leave no doubt that it is the anhydride of meta nitrobenzoic acid. It dissolves readily in dilute alkalies in the cold, and from such solution mineral acids precipitate the meta acid, easily identified by its melting point, 141°, and crystalline form.

Meta nitrobenzoic anhydride is readily soluble in alcohol, ether, and chloroform, less readily in benzol (from which solvent it crystallizes best), and difficultly in water. Cold water has but little effect upon it, boiling water decomposes it rapidly into the free acid.

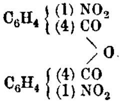
From the gelatinous phosphoric residue by extraction with absolute alcohol, evaporating to dryness, and taking up with water, a product was obtained which crystallized from alcohol in small rhombic plates, melting at 42°. The same body was obtained by treating the anhydride with absolute alcohol and phosphorpentoxide. Its melting point and method of formation show it to be the meta nitrobenzoic ester.

IV. *Action of Phosphorpentoxide upon Para Nitrobenzoic Acid in an Excess of Benzol.*

Para nitrobenzoic anhydride is the principal product when para nitrobenzoic acid and phosphorpentoxide are boiled together for some hours in an excess of dry benzol. The proportions employed were the same as with the ortho and meta nitro acids.

The anhydride crystallizes from benzol in white leaflets melting at 184°. The analyses gave the following: —

0.1716 grm. substance gave 0.3311 grm. CO_2 and 0.0530 grm. H_2O.
0.3461 grm. gave 25.6 c.c. nitrogen at 4.6° and 746.5 mm.

	Calculated for  $\begin{matrix}C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(4)\ CO\end{matrix}\right.\\ \qquad >O\\ C_6H_4\left\{\begin{matrix}(4)\ CO\\(1)\ NO_2\end{matrix}\right.\end{matrix}$	Found
C	53.16	52.61
H	2.53	3.40
N	8.86	8.90

Like the isomeric ortho and meta bodies, the para nitrobenzoic anhydride is an exceedingly difficult substance to burn. It is but slightly soluble in alcohol, ether, benzol and carbon disulphide in the cold, readily however on warming. In ligroine and water it is insoluble. Continued boiling with water converts it into the acid. Alkalies produce the same effect, slowly in the cold, more rapidly on heating.

As in the case of the other nitro-anhydrides the phosphoric residue gave, on extraction with absolute alcohol, the para nitrobenzoic ethyl ester. This may be more readily obtained by boiling the anhydride with phosphorpentoxide in absolute alcohol solution.

It is proposed to extend the study of this phosphorpentoxide reaction to other substituted benzoic acids.

IX.

NOTE ON THE RELATIVE POSITION OF HIGH TEMPERATURE MELTING AND BOILING POINTS.

By Carl Barus.

Presented May 24, 1892.

In my work on the measurement of high temperatures,* I largely availed myself of boiling points for calibration purposes. With the aid of suitable apparatus, ebullition can be maintained for an indefinite length of time, and the boiling point is probably less influenced by the impurities of the substance. Apart from this, one of them — the boiling point of zinc — has been so frequently redetermined by different observers (Becquerel, Deville and Troost, Violle, and myself) as to have become a veritable landmark in the region of high temperature, and guaranteed with an accuracy of about one per cent by actual air thermometry.

Melting points, however, have as a rule been found indirectly, and those most relied upon to-day are due to the unique calorimetric work of Violle. I am not aware that anybody has recently endeavored to compare melting and boiling points with the same pyrometer, and with especial reference to the boiling point of zinc. This I have had occasion to do, and the results of the survey made are unfortunately disappointing.

I made use of a platinum-iridioplatinum thermocouple, which had been compared with the porcelain air thermometer between 300° and 1,200°. The couple was thus found to be quite free from anomalies, and to be quite regular in its thermal variations. It placed the boiling point of zinc at 930°, or at the lowest estimate at 925°, agreeing well with the classic results for this datum referred to.

Now, on using these same couples to determine the melting points of a number of elements, among which silver, gold, and copper need here alone be cited, I found that if Zn boils at 925°, then Ag, Au, and Cu should melt at 985°, 1,093°, and 1,097°, respectively. Conversely, if Ag, Au, and Cu have the Violle melting points 954°, 1,045°, and 1,054°, respectively, then zinc should boil at say 895°, or at least 30° below its apparently well established boiling point.

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* Bulletin U. S. Geological Survey, No. 54, 1889, Chap. II.

These difficulties can only be cleared away by minute inquiry into all the details of experiment involved: for it will be seen that the relative positions of these (and other) melting points are well preserved, and the work already involves variations of method. The discrepancy increases when higher temperatures are approached (palladium, nickel, platinum, etc.), and it gradually vanishes on reaching lower temperatures. In the former case, however, the limits of the air thermometer are overstepped, and all data are somewhat hypothetical.

X.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, WORCESTER, MASS.

ON BIVALENT CARBON.

FIRST PAPER.

By J. U. Nef.

Presented May 11, 1892.

Among the constantly increasing compounds of carbon, there is but one substance in which the presence of a bivalent carbon atom is pretty generally accepted, and which is always put forward as the sole exception to the otherwise constant tetravalence of this element, namely, carbonic oxide. For a substance possessing two free affinities,* $O=C=$, carbonic oxide is however a remarkably inert compound, since it absorbs chlorine only very slowly in diffused light,† and if allowed to stand for weeks in the sunlight with one molecule of bromine, only a very slow and incomplete reaction takes place.‡

Carbonic oxide does not react with iodine or with the haloid acids. It was found by a special experiment that hydriodic acid does not react on carbonic oxide at a temperature of 200°, although, as is well known, this substance adds itself more readily to unsaturated compounds than any of the other haloid acids.

Carbonic oxide is thus much less reactive than the majority of the olefine derivatives, many of which form in the cold, and in the absence of light, addition products with the above named reagents. This fact depends, as I have already shown in the case of acetacetic ether, § on the law that an unsaturated compound forms addition products the more readily, the more positive the condition of the molecule, so that, e. g., ethylene, $CH_2=CH_2$, is more reactive than carbonic oxide, $O=C=$, because the presence of oxygen in the latter substance renders the molecule more negative. For the same reason, the double bond in sodic acetacetic ether,

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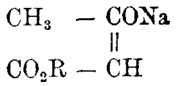
* It is improbable that the two extra affinities in carbonic oxide exist free: they probably polarize, or mutually saturate each other as in ethylene, so that it is legitimate to speak of a *nascent* carbonic oxide.

† Davy, Gilbert's Annalen, XLIII. 296.

‡ Emmerling, Ber. d. Chem. Ges., XIII. 873.

§ Ann. Chem. (Liebig), CCLXVI. 52.



$$\begin{array}{lcl} CH_3 & - & CONa \\ & & \| \\ CO_2R & - & CH \end{array}$$

is much more reactive than in the ordinary olefine derivatives.

Were it possible now to replace the oxygen in carbonic oxide by a bivalent radical which is less negative than oxygen, as, for example, by $(CH_3)_2$, H_2, $R-N=$, $H-N=$, the resulting compounds,

$$\begin{array}{cccc} \text{I} & \text{II} & \text{III.} & \text{IV.} \\ {}^{CH_3}_{CH_3} > C=, & H_2=C=, & R-N=C=, & HN=C=, \end{array}$$

would probably be more reactive than carbonic oxide, and perhaps also than the olefine and acetylene derivatives: the energy of the compounds must also decrease in the order, I.–IV., given.

All attempts to isolate methylene, $H_2C=$, or dichlormethylene, $Cl_2=C=$, have up to the present time been unsuccessful; especially have numerous and zealous experiments been carried out in the hope of isolating the hydrocarbon methylene, $H_2C=$; as, for instance, attempts to split off water from methylalcohol, CH_3OH, by means of phosphorus pentoxide* or concentrated sulphuric acid,† or to split off hydrochloric acid from methylchloride by passing its vapors through red-hot porcelain tubes.‡ These experiments could not however be successful, since the methylene, even if formed, must again unite with the reagents applied or split off.

A most interesting experiment in this direction was carried out by Butlerow,§ who found that when methylene iodide, CH_2I_2, is heated in a sealed tube at 100° with copper and water, there is formed ethylene, $CH_2=CH_2$, and cuprous iodide. This experiment cannot, however, be considered as proving that methylene is not capable of existence, because already many unsaturated compounds, especially the acetylene derivatives, show a great tendency to polymerize, and it is therefore highly probable that such an energetic substance as methylene must be expected to be might polymerize at 100°.

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* Dumas, Annales de Chim. et de Phys., LVIII. 128.

† Regnault, Annales de Chim. et de Phys., LXXI. 427.

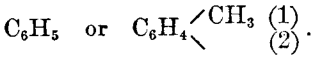
‡ Perrot, Ann. Chem. (Liebig), CI. 375.

§ Ann. Chem. (Liebig), CXX. 356.

Although methylene or its homologues have not as yet been isolated, there are a number of known substances which possibly may contain bivalent carbon, as, for instance, prussic acid, $HN{=}C{=}$, its salts, and the so called carbylamines, $R{-}N{=}C{=}$, or isonitriles, which were discovered by Gautier [*] and Hofmann.[†] I have therefore undertaken, in the first place, a very thorough study of these substances, in order to prove by experiment, if possible, whether bivalent carbon is present or absent; and in case bivalent carbon is present, and its properties thus have become more exactly known, to attempt further the isolation of methylene or of its homologues; the latter substances naturally may be expected to be still more reactive than prussic acid or the carbylamines.

From the experiments which I have the honor to present to the Academy in this first paper, it will be seen that the presence of bivalent carbon in the carbylamines, $RN{=}C{=}$, has been proved with great precision, and, further, it has become very probable that prussic acid has the formula $H{-}N{=}C{=}$. The carbylamines are far more reactive than the ordinary olefine and acetylene derivatives, but they do not yet equal sodic acetacetic ether in energy of reaction. Prussic acid, on the other hand, shows, as far as can be judged now, a reactivity which is not much different from that shown by the ordinary unsaturated compounds, — facts which are entirely in accord with the ideas developed above.

The experiments on the isonitriles have been carried out principally with phenyl and *o*-tolylisocyanide. The following addition products have been obtained thus far, and their constitution proved. The reactions are given using the general expression $R{-}N{=}C{=}$, where R denotes either



$$C_6H_5 \quad \text{or} \quad C_6H_4\begin{matrix}\diagup CH_3 & (1) \\ \diagdown & (2)\end{matrix}.$$

1. Halogens (X_2) react at —15°, with great evolution of heat, as follows:

$$R{-}N{=}C{=} + X_2 = RN{=}C{=}X_2.$$

2. Hydrochloric acid reacts with explosive violence at —15°, which is avoided, as in case 1, by suitable dilution, and there are formed addition products of the general formula:

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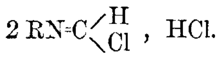
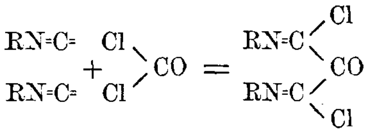
[*] Annales de Chim. et de Phys., [4.], XVII. 205.

[†] Ann. Chem. (Liebig), CXLIV. 114, CXLVI. 107.



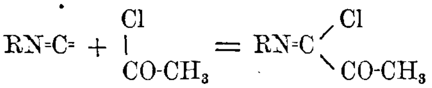
$$2\,RN{=}C{\begin{smallmatrix}/H\\ \backslash Cl\end{smallmatrix}},\ HCl.$$

3. Phosgene reacts slowly at −15°, forming quantitatively mesox-alkylimidechlorides:



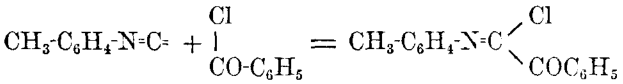
$$\begin{matrix}RN{=}C{=}\\ \\ RN{=}C{=}\end{matrix} + \begin{matrix}Cl\\ \\ Cl\end{matrix}{>}CO = \begin{matrix}RN{=}C{\begin{smallmatrix}/Cl\\ \backslash\end{smallmatrix}}\\ CO\\ RN{=}C{\begin{smallmatrix}/\\ \backslash Cl\end{smallmatrix}}\end{matrix}$$

4. Heated for a few minutes at 100°, acetylchloride adds itself quantitatively as follows:



$$RN{=}C{=} + \begin{matrix}Cl\\ |\\ CO{-}CH_3\end{matrix} = RN{=}C{\begin{smallmatrix}/Cl\\ \backslash CO{-}CH_3\end{smallmatrix}}$$

5. Benzoylchloride adds itself slowly at 100° to *o*-tolylisocyanide, and benzoylformic-*o*-tolylimidechloride is formed:

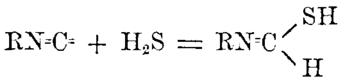


$$CH_3{-}C_6H_4{-}N{=}C{=} + \begin{matrix}Cl\\ |\\ CO{-}C_6H_5\end{matrix} = CH_3{-}C_6H_4{-}N{=}C{\begin{smallmatrix}/Cl\\ \backslash COC_6H_5\end{smallmatrix}}$$

6. On heating with sulphur at 130°, the isonitriles are converted quantitatively into the corresponding mustard oils:

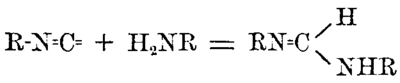
$$RN{=}C{=} + S = RN{=}C{=}S.$$

7. Sulphuretted hydrogen reacts at 100°, and forms alkylthioformamides:



$$RN{=}C{=} + H_2S = RN{=}C{\begin{smallmatrix}/SH\\ \backslash H\end{smallmatrix}}$$

8. Heated for a short time with primary amines, RNH_2, at 180°–220°, the isonitriles are converted into formamidine derivatives:



$$R{-}N{=}C{=} + H_2NR = RN{=}C{\begin{smallmatrix}/H\\ \backslash NHR\end{smallmatrix}}$$

The isonitriles are converted by means of nascent hydrogen into secondary amines, $RNH{-}C{-}H_3$: an intermediate product, $RN{=}CH_2$, has not as yet been isolated. The isonitriles used were made according to Hofmann's method * from primary amines, caustic potash, and chloroform. Hofmann isolated only two products, namely, phenyl and isoamylisocyanide, the first named substance, as will be seen later, was not pure nor entirely free from aniline. It was therefore necessary, in the first place, to find an exact method for separating isonitriles from primary amines, which was readily accomplished. It depends simply on the fact that the isonitriles are not basic substances, so that, for example, an ethereal solution of aniline and phenylisocyanide can be separated completely by shaking once with a solution of dilute hydrochloric acid. It follows, therefore, that the hitherto accepted strong basic property of the isonitriles is a mistake, and the energy with which these substances unite with haloid acids depends, not on their basic nature, but on the presence of bivalent carbon.

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* Ann. Chem. (Liebig), CXLIV. 114.

Gautier,* to whom unquestionably belongs the priority in the discovery of the isonitriles, introduced the name *carbylamines* for them because of their supposed strong basic properties. He regarded them as ammonia in which one hydrogen atom was replaced by alkyl, while the other two were replaced by C'', $\left.\begin{matrix}R\\C''\end{matrix}\right\{N^{III}$, and supposed them to react with the haloid acids like ammonia, going over thus from trivalent into pentavalent nitrogen, $\left.\begin{matrix}R\\C''\end{matrix}\right\}N^{V}$, HX. This was the chief reason that led him to disregard the other possible formula, $\left.\begin{matrix}R\\C^{IV}\end{matrix}\right\{N^{V}$, for the isonitriles.

In a similar manner Gautier † regarded the alkyl-cyanides (ammonia, *in which the three hydrogen atoms are replaced by trivalent* $R\text{-}C^{\equiv}$) as weak bases, because they unite with gaseous hydrochloric

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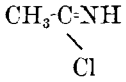
[*] Annales de Chim. et de Phys., [4.], XVII. 205. I cite here exclusively from Gautier's paper in Annales de Chimie et de Physique, [4.], XVII. 103–260 (1869), which includes the following previous papers:

Ann. Chem. (Liebig),	138.38	142.294	145.118	146.119, 352	149.29, 155	151.239	152.221
Bull. de la Soc Chim.,	4.88					11.214	11.222
Comptes Rendus,		63.920	65.410	65.468-72 65.862	66.1214 67.723, 804		

In this paper Gautier describes the compounds more fully, and corrects a number of his previous statements. The statements of Gautier on prussic acid, the nitriles and carbylamines in Beilstein, and other treatises on organic chemistry, are therefore incomplete, since remarkably enough this last paper has not been taken into consideration. I regret that the Thèse of Gautier (Paris, 1869), which may possibly contain still more details, has not been accessible to me.

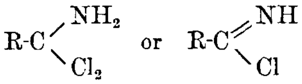
† Ibid., pp. 111, 118.

and hydrobromic acid. We know now, because of the experiments of Michael and Wing,[*] that the resulting compounds are not salts, but addition products: acetonitrile, for example, forms with hydrochloric acid



$$\begin{array}{l} CH_3\text{-}C{=}NH \\ \qquad\ \ \diagdown \\ \qquad\quad Cl \end{array}$$

It is now pretty generally conceded, especially also because of Wallach's[†] experiments, that hydrochloric acid forms with alkylcyanides either amide or imidechlorides,



$$R\text{-}C\begin{cases} NH_2 \\ Cl_2 \end{cases} \quad \text{or} \quad R\text{-}C\begin{cases} NH \\ Cl \end{cases}$$

Gautier[‡] has brought forward as a further proof for his carbylamine formula the fact that methyl and ethyl cyanate are formed by the oxidation of methyl and ethylisocyanide respectively. These oxidation products, however, are formed as side products, the chief products being very complicated compounds, as $C_7H_{12}N_2O_4$ and $C_8H_{12}N_4O_5$ (from CH_3NC), and $C_9H_{22}N_4O_2$ as well as $C_{13}H_{25}N_5O_4$ (from C_2H_5NC).

It seems to me, therefore, that this reaction cannot be regarded as sufficient to decide the constitution of the isonitriles, since it is likely that a substance having the constitution $RN^{V}{\equiv}C^{IV}$ may also give alkylcyanate, $RN{=}C{=}O$, by oxidation.

The chief argument of Gautier for his carbylamine formula, $\begin{matrix}R\\C''\end{matrix}\Big\{N^{III}$, namely, the supposed strong basic properties of the compounds, has already been proved untenable. Furthermore, the present views with regard to the nature of the isonitriles differ; whereas some chemists[§] consider the presence of bivalent carbon as possible; others, as Hofmann,[||] V. Meyer and Jacobson,[¶] v. Richter,[**] favor the formula $R\text{-}N{\equiv}C$, while Beilstein[††] simply writes RNC.

The above briefly stated facts, which are given in detail in the following experimental portion, are sufficient to furnish the complete proof that the isonitriles possess the constitution represented by the formula $R{-}N{=}C{=}$: furthermore, the name carbylamine is no longer justifiable for this class of compounds, because the members are not bases, as this name represents.

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[*] Amer. Chem. Journal, VII. 72.

[†] Ann. Chem. (Liebig), CLXXXIV. 1, CCXIV. 192.

[‡] *Loc. cit.*, XVII. 228, 242, 255.

[§] Graham Otto, Lehrbuch der org. Chemie, neue Ausgabe von Kolbe und E. v. Meyer.

[||] Ber. d. chem. Ges., X. 1095.

[¶] Lehrbuch der org. Chemie, I. 252.

[**] Ibid., translation by E. F. Smith, p. 287.

[††] Handbuch der org. Chemie, I. 1173, Zweite Aufl.

Experimental Part.

I. *On Phenylisocyanide,* $C_6H_5N{=}C{=}$.

Preparation of Phenylisocyanide. — To a solution of 240 grams caustic potash in 800 c.c. alcohol (99%) is added slowly, by means of a drop funnel, a solution of 100 grams aniline in 214 grams chloroform. Reaction sets in at first with great violence, so that the solution soon reaches its boiling point. It is therefore necessary to cool continually, and the temperature is best kept at about 50°, because, if cooled too much, reaction sets in all at once, and with violence. After standing for a short time, during which complete reaction slowly takes place, and much potassic chloride has separated out, the alcohol is distilled off * on a water bath, and a litre of hot water poured over the residue, in order to dissolve the potassic chloride. On cooling, the upper oily layer, consisting of aniline and phenylisocyanide, is drawn off, and the aqueous solution extracted with ether. The ethereal solution is washed with 120 grams hydrochloric acid (sp. gr. 1.15), previously diluted to a litre; this is best done in two portions, using three fourths at first, and then the remainder. By this treatment all the unchanged aniline, as well as some diphenylformamidine formed, go into the acid solution, while the phenylisocyanide remains dissolved in the ether. The ether is distilled off without first drying it, and the dark brown colored residue distilled with steam. Phenylisocyanide is carried over very quickly as a colorless oil, which on standing soon becomes colored pale green. It is again extracted with ether after adding a small amount of dilute sulphuric acid, and the ethereal solution dried with caustic potash, and, after getting rid of the ether, the dark blue residual oil is distilled under reduced pressure. Phenylisocyanide boils at 64° at 20 mm., at 71° at 30 mm., at 78° at 40 mm. pressure, leaving a slight blue residue (polymeric product).

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* Small amounts of aniline and isonitrile are carried over with the alcohol, which, however, it is not worth while to work up. It is not possible to use the alcohol over again, since it contains chloroform.

The distillate, as above with steam, is at first perfectly colorless, but becomes light blue in a few minutes, and in an hour is changed to a deep dark blue liquid, which gets darker and darker; in the course of a few weeks it becomes viscous, and at the same time purple red needles begin to appear. After three months standing, the whole mass is changed to a solid resin, which, brought on clay plates and pulverized, goes over into a brown powder. This is probably a polymeric product, and from the above it is evident that phenylisocyanide is an extremely unstable substance. For all the reactions mentioned in this paper freshly distilled phenylisocyanide must therefore be used. At higher temperatures, already at 100°, polymerization takes place very quickly. At ordinary pressure phenylisocyanide boils at 165°–166°, and although at first a small portion goes over colorless, much polymerization takes place.

Hofmann's product evidently contained some aniline, since he says * that on distillation it is converted into an odorless substance crystallizing in needles and partly volatilizing at 230°. The latter substance was in all probability diphenylformamidine formed by the action of the aniline present on phenylisocyanide (see below). Weith † obtained the same substance on heating phenylisocyanide in sealed tubes at 220°.

The isonitriles ‡ all burn with very great difficulty,§ because of the formation of polymeric products, and it was possible to obtain good analytical results only by mixing with lead chromate. The nitrogen determinations also come low, unless the substance is mixed with copper oxide, and heated long and very hard (see analyses I. and II.).

0.1145 gram substance gave 0.3411 gram CO_2 and 0.0554 gram H_2O.

0.1452 gram substance gave 16.2 c.c. moist nitrogen at 18° and 757 mm.

0.1803 gram substance gave 22 c.c. moist nitrogen at 20° and 754 mm.

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* Ann. Chem. (Liebig), CXLIV. 118.

† Ber. d. chem. Ges., VI. 213.

‡ Hofmann, Ann. Chem. (Liebig), CXLIV. 117, has analyzed phenylisocyanide, but he gives no analytical data.

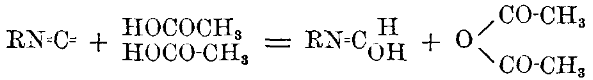
§ It is therefore possible that azulmic acid, which is formed by the polymerization of prussic acid, is free from oxygen, especially since no concordant results have been obtained in its analysis by different chemists. Cf. Gautier, *loc. cit.*, XVII. 158 and 161.

	Theory for C_7H_5N.	Found. I.	Found. II.
C	81.55	81.25	
H	4.85	5 37	
N	13.60	12.84	13.84

Phenylisocyanide is lighter than water, specific gravity 0.977 at 15° (Westphal). It possesses a horrible smell, a bitter taste, and causes headaches and flow of the saliva. Continued inhalation of its vapors produces nausea, and nervous exhaustion.*

Nascent hydrogen converts it into monomethylaniline: 10 grams were dissolved in 90 grams amylalcohol, 6 grams of sodium added, and the mixture heated to boiling until the sodium had disappeared. The smell of isocyanide was no longer present, and after washing the amylalcohol with water it was treated with dilute hydrochloric acid, and the acid solution evaporated one half on a water bath, and then made alkaline: the oil which separates out was extracted with ether, and dried with anhydrous sulphate of copper. On fractional distillation, 7 c.c. of an oil, boiling from 187°–191°, were obtained, which treated in acid solution with sodic nitrite gave the well known methylaniline nitroseamine. This was converted back again by means of tin and hydrochloric acid into monomethylaniline (bpt. 189°–192°); the latter substance finally treated with acetic anhydride, and thus 4 grams of methylacetanilide (mpt. 99°) were obtained. These reactions were so conclusive that an analysis of the monomethylaniline was considered superfluous.

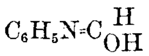
Gautier † has shown that methyl- and ethyl-isocyanide react with acetic acid as follows:



$$RN{=}C{=} + \begin{matrix}HOCOCH_3\\ HOCO\text{-}CH_3\end{matrix} = RN{=}C\begin{matrix}H\\ OH\end{matrix} + O\begin{matrix}\diagup CO\text{-}CH_3\\ \diagdown CO\text{-}CH_3\end{matrix}$$

Alkyl Formamide.

Phenylisocyanide reacts with acetic acid (2 molecules) slowly at ordinary temperature, forming acetic anhydride and formanilide,



$$C_6H_5N{=}C\begin{matrix}H\\ OH\end{matrix}$$

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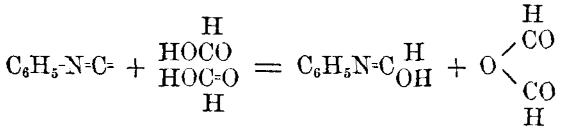
* Gautier states, *loc. cit.*, XVII. 218, that methyl and ethylisocyanide are not really to be regarded as poisonous substances, since several drops of either when put in the eyes or mouth of a dog had absolutely no effect, and even 0.5 gram put on an open wound produced no apparent effect. He states, however, that they have a marked effect on the human system.

† *Loc. cit.*, XVII. 223 and 241.

which can be easily separated by fractional distillation under reduced pressure: the former substance was then identified by its boiling point (137°), but the formanilide obtained is never pure, but contains a considerable quantity of acetanilide from which it can be separated by recrystallization from ligroine and benzene. This is due to the fact that formanilide, as shown by a special experiment, is converted almost entirely in half an hour at 90° by acetic anhydride into acetanilide.

A new experiment was therefore tried, using formic acid instead of acetic acid, in the hope of obtaining thereby formic anhydride which has not yet been isolated.

On mixing phenylisocyanide with pure formic acid (mpt. 8°.6) at 0°, a very violent reaction takes place, with much evolution of gas: the phenylisocyanide was therefore slowly poured into well cooled formic acid (2 molecules), whereby immediately at 0° a steady evolution of pure carbonic oxide takes place. On distilling the residue, only formanilide was obtained, which boils at 283°–285° almost without decomposition, and, recrystallized from ligroine, melts at 48°. The product obtained is identical in every respect with a formanilide made according to the method of Wallach and Wüsten.* This experiment shows that formic anhydride, which probably is formed as an intermediate product,



$$C_6H_5\text{-}N\text{=}C\text{=} + \begin{array}{c}H\\ HOCO\\ HOC\text{=}O\\ H\end{array} = C_6H_5N\text{=}C\begin{array}{l}H\\ OH\end{array} + O\begin{array}{l}\quad H\\ \diagup CO\\ \diagdown CO\\ \quad H\end{array}$$

is not capable of existence at 0°, but decomposes spontaneously into 2 CO and H_2O. Gerhardt † has already attempted, without success, to obtain this substance from benzoylchloride and sodic formiate. The following further observation was then made in this direction. On pouring phosphorus oxychloride (1 molecule) over potassic formiate (4 molecules), a violent reaction takes place at 0°, and much carbonic oxide is evolved.

On adding anhydrous oxalic acid to phenylisocyanide, reaction takes place at 0° and formanilide, carbonic oxide, and carbon dioxide are formed, which makes it likely that oxalic anhydride, probably formed as an intermediate product, decomposes spontaneously.

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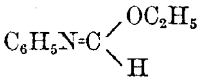
* Ber. d. chem. Ges., XVI. 145.

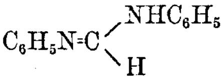
† Ann. Chem. (Liebig), LXXXVII. 149.

On heating phenylisocyanide for six hours in a sealed tube at 130° with an alcoholic solution of sodium ethylate (1 molecule), there is formed in large quantity diphenylformamidine * (mpt. 138°). The formation of this substance is explained most simply by assuming that in the presence of sodium ethylate alcohol adds itself to the phenylisocyanide, forming phenylformimidoether,



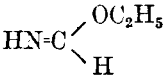
$$C_6H_5N{=}C\begin{array}{l}\diagup OC_2H_5\\ \diagdown H\end{array}$$

That such substances go over into diphenylformamidine,



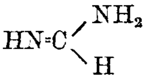
$$C_6H_5N{=}C\begin{array}{l}\diagup NHC_6H_5\\ \diagdown H\end{array}$$

with remarkable ease is evident from the work of Comstock and Kleeberg; † and Pinner ‡ also has shown how easily formimidoether,



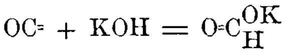
$$HN{=}C\begin{array}{l}\diagup OC_2H_5\\ \diagdown H\end{array}$$

goes over into formamidine,



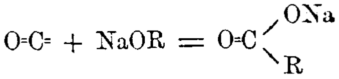
$$HN{=}C\begin{array}{l}\diagup NH_2\\ \diagdown H\end{array}$$

Experiments undertaken with the object of adding sodium ethylate or methylate to phenyl- or *o*-tolylisocyanide have so far been unsuccessful, because on heating in sealed tubes at 130°, much polymerization takes place. Such an addition would be especially interesting, because carbonic oxide, $O{=}C\langle$, according to Berthelot,§ directly adds caustic potash,



$$OC{=} + KOH = O{=}C\begin{array}{l}OK\\ H\end{array}$$

and, according to Geuther and Fröhlich,‖ also sodium methylate and ethylate,



$$O{=}C{=} + NaOR = O{=}C\begin{array}{l}\diagup ONa\\ \diagdown R\end{array}$$

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* Hofmann, Jahresber. 1858, p. 354.

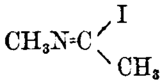
† Amer. Chem. Journal, XII. 498.

‡ Ber. d. chem. Ges., XVI. 354 and 1644.

§ Ann. Chem. (Liebig), XCVII. 125.

‖ Ann. Chem. (Liebig), CCII. 290.

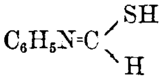
Gautier[*] noticed that methylisocyanide reacts with methyliodide, and forms, besides much resinous matter, a product soluble in water. That in this case no addition product,



$$CH_3N{=}C\left\langle\begin{matrix}I\\CH_3\end{matrix}\right.$$

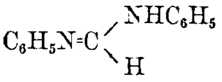
has been formed, but that polymerization has taken place, follows from the work of Ljubjawin,[†] who studied this reaction more closely. It follows further from the investigations of Wallach,[‡] that a substance of the above nature must be very unstable, if indeed capable of existence; and that it would probably lose hydriodic acid and go over into basic products. I found, as did Ljubjawin in the case of ethylisocyanide, that on heating phenylisocyanide with ethyliodide at 100° exclusively polymerization takes place.

That phenylisocyanide reacts with hydrogen sulphide, forming thioformanilide,



$$C_6H_5N{=}C\left\langle\begin{matrix}SH\\H\end{matrix}\right.$$

has been shown by Hofmann[§]; that it reacts with sulphur to form phenylmustard oil, $C_6H_5N{=}C{=}S$, has been made probable by the experiments of Weith,[||] who obtained sulphocarbanilide on heating phenylisocyanide containing aniline with sulphur. Weith[¶] has also shown that on heating aniline and phenylisocyanide in sealed tubes at 220°, diphenylformamidine



$$C_6H_5N{=}C\left\langle\begin{matrix}NHC_6H_5\\H\end{matrix}\right.$$

is formed. I can confirm his experiments, and obtained 30% yield in this case.

On pouring phenylisocyanide over dry silver oxide, or mercuric oxide, an extremely energetic reaction takes place: an ethereal solution of the isonitrile, with one molecule of mercuric oxide, heated to about 60° in a sealed tube, exploded with great violence. On heating the same mixture gently on a water bath with reversed condenser, reduction of the mercuric oxide is noticed at 40°, and also the characteristic smell of phenylcyanate observed. The quantity of this substance formed was very small, and a large amount of gaseous products appear, so that it would necessitate the sacrifice of too much material in order to obtain sufficient phenylcyanate for an analysis. The experiments were therefore not continued, especially as Gautier * has already accomplished this in the case of methylisocyanide.

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[*] *Loc. cit.*, XVII. 226.

[†] Ber. d. chem. Ges., XVIII. R. 407.

[‡] Ann. Chem. (Liebig), CLXXXIV. 86 and 108, CCXIV. 221.

[§] Ber. d. chem Ges., X. 1095.

[||] Ibid., VI. 210.

[¶] Ibid., IX. 454.

Isocyanphenylchloride, or Phenylimidocarbonylchloride, $C_6H_5N = C{-}Cl_2$.

On passing dry chlorine into a well cooled solution of phenylisocyanide in five to six times its volume of chloroform, the gas is absorbed instantly and completely, without the slightest trace of hydrochloric acid being formed. The reaction is complete when the color of the solution changes suddenly from blue to yellow. The chloroform solution is washed immediately with dilute sodic hydrate, dried with calcic chloride, and then fractionated. A colorless oil is obtained boiling at 204°–205° (uncorr.), or at 209°–210° (thermometer entirely in the vapor).

0.2740 gram substance gave 0.4822 gram CO_2 and 0.0755 gram H_2O.

0.0779 gram substance gave 0.1298 gram AgCl on ignition with CaO.

	Theory for $C_7H_5NCl_2$.	Found.
C	48.27	47.99
H	2.88	3.06
Cl	40.80	41.22

Isocyanphenylchloride is a colorless, sharp-smelling oil, which attacks the eyes strongly. On heating it with acetic acid, acetanilide is formed; with water, s. diphenylurea; with silver oxide, phenylcyanate; with alcohol, phenylurethane. On heating it with aniline, all at once a very violent reaction takes place, which can only be regulated by taking small quantities (about 2 grams). There is left a white mass, the hydrochloride of a base, which crystallizes from dilute alcohol in colorless scales, melting at 241°. On addition of ammonia to an aqueous solution of the salt, the free base separates out. After being twice recrystallized from alcohol, it showed the melting point 143°, and was identical in every respect with the long known α-triphenylguanidine,*

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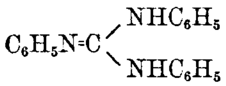
* *Loc. cit.*, XVII. 229.



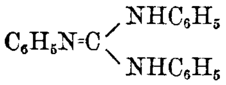
$$C_6H_5N{=}C\begin{cases}NHC_6H_5\\NHC_6H_5\end{cases}$$

Hence the constitution of the dichloride, $C_6H_5N = C{=}Cl_2$, is proved. An analysis of the guanidine derivative gave the following result:

0.1981 gram substance, dried at 105°, gave 0.5770 gram CO_2 and 0.1121 gram H_2O.

	Theory for $C_{19}H_{17}N_3$.	Found.
C	79.44	79.43
H	5.93	6.28

The above mentioned reactions and properties of isocyanphenylchloride show in many respects coincidence with an isocyanphenylchloride, which Sell and Zierold † have obtained from phenylmustard oil and chlorine; only as regards boiling point and behavior towards aniline is there a difference. Sell and Zierold give the boiling point 211°–212°, and state that the oil is yellow; they obtained further on treatment with aniline, besides much resinous matter, the hydrochloride of an isomeric triphenylguanidine, which melts at 207°, and contains half a molecule of crystal water. They state that a carbon and hydrogen, as well as nitrogen determination of the salt gave figures ‡ agreeing exactly for a base,



$$C_6H_5N{=}C\begin{cases}NHC_6H_5\\NHC_6H_5\end{cases}$$

They did not succeed in isolating the free base, as rapid resin formation was noticed in attempts to set it free. I have succeeded in clearing up these differences: the product described by Sell and Zierold as isocyanphenylchloride was a mixture of isocyanphenylchloride and chlorinated isocyanphenylchlorides, $Cl{-}C_6H_4{-}N{=}CCl_2$. A number of observations given in the paper of the chemists named point towards this: they obtained, e. g., on treating the crude product with ammonia, a substance which they consider to be

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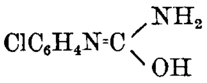
* Merz and Weith, Zeitschr. für Chemie, 1868, p. 513.

† Ber. d. chem. Ges., VII. 1228.

‡ Sell and Zierold give no analytical data, nor do they state with what salt, whether $C_{19}H_{17}N$, 2 HCl, or $C_{19}H_{17}N$, HCl, the analyses agree.



$$ClC_6H_4N=C\begin{cases}NH_2\\OH\end{cases}$$

because on treatment with caustic potash it is converted into chloraniline.

The product described as isotriphenylguanidine hydrochloride (mpt. 207°) was either the salt of a chlorinated triphenylguanidine, or perhaps still a mixture.

Sell and Zierold state that on passing chlorine gas into phenylmustard oil no substitution takes place; it follows that probably, on fractionating the products of the reaction, $C_6H_5N=CCl_2+SCl_2$, chlorine is set free,* and then substitution takes place. That this is so is proved by the following experiment, which leads to pure isocyanphenyl chloride. 100 grams of phenylmustard oil were treated according to the directions given by Sell and Zierold with chlorine, and, as soon as no more absorption of the gas is noticed, the chloroform solution is poured slowly, with thorough shaking, into much water, in order to decompose the SCl_2 formed. The chloroform solution, after treating with sodic hydrate, is dried with calcic chloride, and on fractional distillation a colorless oil obtained boiling at 204°–205° (80 grams), which is identical in every particular with the product obtained from phenylisocyanide and chlorine. On treatment with aniline it is converted into triphenylguanidine hydrochloride (mpt. 241°). The free base obtained therefrom melts at 143°, and a nitrogen determination gave the following result: —

0.2142 gram substance, dried at 105°, gave 27.5 c.c. moist nitrogen at 19°, and 748 mm.

	Theory for $C_{19}H_{17}N_3$.	Found.
N	14.63	14.52

An analysis of the isocyanphenylchloride obtained from phenylmustard oil and chlorine gave the following results: —

0.1542 gram substance gave 0.2725 gram CO_2 and 0.0431 gram H_2O.

0.3003 gram substance gave 21.1 c.c. moist nitrogen at 20° and 756 mm.

0.1052 gram substance gave 1754 gram AgCl on ignition with CaO.

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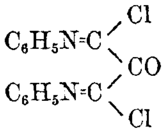
* SCl_2 is decomposed by distillation, as is well known, into S_2Cl_2 and Cl_2.

	Theory for $C_7H_5NCl_2$.	Found.
C	48.27	48.19
H	2.88	3.15
N	8.05	7.99
Cl	40.80	41.24

On treating phenylisocyanide in chloroform solution with one molecule of bromine at 0°, absorption takes place instantly without a trace of hydrobromic acid being formed; after distilling off the chloroform, a yellow oil, probably $C_6H_5N{=}CBr_2$, remains, which could not be distilled in vacuum, nor be otherwise purified.* On adding to a solution of phenylisocyanide in carbon bisulphide, a carbon bisulphide solution of iodine (1 molecule), immediate decolorization of the iodine is noticed, as well as a marked evolution of heat, and a dark yellow oil, probably the iodide, $C_6H_5N{=}CI_2$, obtained.

Mesoxanilid-imidechloride,



$C_6H_5N{=}C(Cl){-}CO{-}C(Cl){=}NC_6H_5$

To 5 c.c. phenylisocyanide, cooled to —20°, are added 5 c.c. of phosgene † (cooled to —20°), and the mixture protected by calcic chloride tubes from moist air. After standing for an hour at —20°, the mixture is taken out of the freezing solution until the temperature has risen to about 0°, and then cooled again, etc., until no spontaneous evolution of heat is noticed. The experiment cannot well be carried out with larger quantities than given above: 16 c.c., e. g., of a mixture in a tube cooled with ice and salt reacted all at once, while attempting to seal it up, so energetically that half the mixture was thrown out of the tube.

Several portions treated as above mentioned were therefore united, and the excess of phosgene removed by heating on a water bath, and the residual oil, which contains no trace of isonitrile, fractionated under diminished pressure. A viscous hygroscopic yellow oil is obtained, having an acid and at the same time an agreeable smell, which boils with slight decomposition at 145°–152° at 15–20 mm. pressure.

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* Tscherniak, Bull. de la Soc. Chim., XXX. 185, obtained in a similar manner, by treating methylisocyanide with bromine, a yellow unstable oil, which could not be purified, and which he did not study further.

† The same result is obtained on pouring the isonitrile into the phosgene.

0.2490 gram substance gave 0.5216 gram CO_2 and 0.0721 gram H_2O.

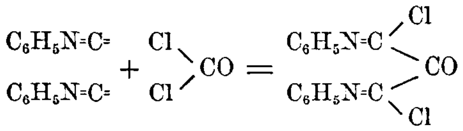
0.3001 gram substance gave 22 c.c. moist nitrogen at 17° and 760 mm.

0.1789 gram substance gave 0.1857 gram AgCl (Carius).

	Theory for $C_{15}H_{10}N_2Cl_2O$.	Found.
C	59.01	57.13
H	3.29	3.22
N	9.18	8.51
Cl	23.12	25.68

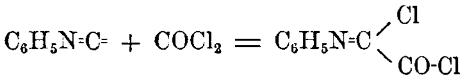
Although the above analytical figures do not agree exactly with the theoretical ones, it is highly probable that the substance is mesoxanilidimidechloride, especially because of the almost quantitative conversion into mesoxanilide (mentioned below). It is most likely that the oil still contained traces of phosgene, since it was distilled only once. Furthermore, Wallach in his well known researches on imide and amidechlorides * very seldom obtained good analytical results, because of the instability of these compounds, even when the substances were obtained in the crystalline form.

Mesoxanilidimidechloride has thus been formed quantitatively according to the following equation:



$$\begin{matrix} C_6H_5N{=}C{=} \\ C_6H_5N{=}C{=} \end{matrix} + \begin{matrix} Cl \\ Cl \end{matrix}\!\!>CO = \begin{matrix} C_6H_5N{=}C<^{Cl} \\ C_6H_5N{=}C<_{Cl} \end{matrix}\!\!>CO$$

That in this case not a trace of oxanilchloride imidechloride is formed, according to the equation



$$C_6H_5N{=}C{=} + COCl_2 = C_6H_5N{=}C<^{Cl}_{CO\text{-}Cl}$$

is shown below under mesoxanilide.

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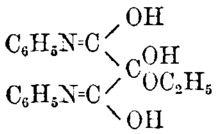
* Ann. Chem. (Liebig), CLXXXIV. 9.

MESOXANILIDE AND ITS DERIVATIVES.

Mesoxanilid-alcoholate = Monoethylether of Dioxymalonic Anilide,



Mesoxanilidimidechloride takes up water slowly from the air and becomes solid. On pouring a large amount of water over the oil, and stirring with a glass rod, all at once reaction sets in, with marked evolution of heat, and the mass solidifies; in order to decompose mechanically enclosed material, it is converted by means of a pestle into a fine powder. The grayish white residue consists of almost pure mesoxanilidehydrate, and equals in weight the phenylisocyanide taken in the first place. It was generally made directly from the crude, not distilled mesoxanilidimidechloride. In order to purify this, it was recrystallized twice from *boiling* alcohol, which converts the hydrate into the alcoholate.

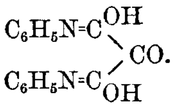
0.1686 gram substance dried over H_2SO_4 in vacuum gave 0.4077 gram CO_2 and 0.0896 gram H_2O.

0.2074 gram substance gave 16.7 c.c. moist nitrogen at 16° and 742 mm.

	Theory for $C_{17}H_{18}N_2O_4$.	Found.
C	64.97	65.94
H	5.73	5.90
N	8.92	9.11

Mesoxanilid-alcoholate is readily soluble in hot, but only slightly so in cold alcohol, and crystallizes out in colorless silky needles. On heating it in a capillary tube it begins to get yellow at 100°, and melts with gas evolution (alcohol) at 145° to 151°, according as the temperature is raised slowly or quickly. In boiling alcoholic or benzine solution, the alcoholate dissociates to a marked extent, and the solutions are colored pure yellow, but on cooling, already at 50° they become colorless. This explains why in the above analysis the per cent of carbon found was somewhat high. The alcoholate dissolves in dilute sodic hydrate and slightly in hot water whereby, however, it is converted into mesoxanilidehydrate.

Mesoxanilide,



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \qquad\qquad\quad \rangle CO. \\ C_6H_5N{=}C_{OH} \end{array}$$

This substance is formed by long heating of mesoxanilidehydrate, or alcoholate, first at 100°, then at 108°–116°, whereby the alcohol or the water respectively goes off very slowly as is seen by the following figures: —

0.9470 gram alcoholate lost, after heating 3½ hours at 100°, 0.0634 gram.
0.9470 gram alcoholate lost, after heating 4 hours at 108°–113°, 0.1240 gram.
0.9470 gram alcoholate lost, after heating 3 hours at 113°–115°, 0.1322 gram.
0.9470 gram alcoholate lost, after heating 3 hours at 116°, 0.1350 gram.
0.9470 gram alcoholate lost, after heating 2½ hours at 109°, 0.1352 gram.

Heated altogether 16 hours, until constant weight was obtained.

Theory for Loss of 1 Molecule Alcohol.	Found.
14.65	14.28

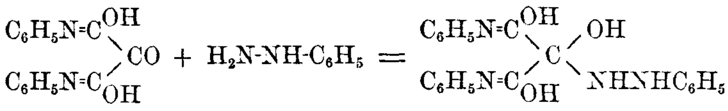
The analysis of the yellow powder thus obtained gave the following results: —

0.1546 gram substance gave 0.3841 gram CO_2 and 0.0661 gram H_2O.
0.2086 gram substance gave 19.5 c.c. moist nitrogen at 17° and 743 mm.

	Theory for $C_{15}H_{12}N_2O_3$.	Found.
C	67.28	67.75
H	4.48	4.75
N	10.45	10.60

Mesoxanilide is soluble without change only in such solvents as contain no alcohol or water; on pouring water or alcohol over it and warming gently, it becomes colorless, forming the alcoholate or the hydrate. The substance, in fact, shows a great resemblance to chloral, which also contains a very reactive carbonyl group.

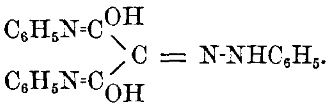
On treating an anhydrous benzine solution of mesoxanilide with phenylhydrazine, it becomes colorless at first, and then a voluminous white precipitate separates out, which, heated to 100°, goes over with loss of water into mesoxanilide-phenylhydrazone described below. In this case, therefore, a simple addition of phenylhydrazine to the carbonyl group takes place,



$$\left.\begin{array}{l}C_6H_5N{=}C^{OH}\\C_6H_5N{=}C_{OH}\end{array}\right\rangle CO + H_2N\text{-}NH\text{-}C_6H_5 = \left.\begin{array}{l}C_6H_5N{=}C^{OH}\\C_6H_5N{=}C_{OH}\end{array}\right\rangle C\left\langle\begin{array}{l}OH\\NHNHC_6H_5\end{array}\right.$$

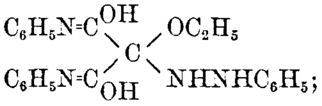
analogous to the action of ammonia on chloral.* On heating mesoxanilide with acetic anhydride reaction takes place just as in case of chloral,† and a colorless substance crystallizing in needles, and melting at 190° is formed: —

Mesoxanilide-phenylhydrazone,



$$\left.\begin{array}{l}C_6H_5N{=}C^{OH}\\C_6H_5N{=}C_{OH}\end{array}\right\rangle C = N\text{-}NHC_6H_5.$$

On adding to a warm alcoholic solution of mesoxanilid-alcoholate one molecule of phenylhydrazine, there is formed almost immediately a voluminous white precipitate, which, filtered off and put on clay plates, is converted into a white powder. This is the hydrazone alcoholate,



$$\left.\begin{array}{l}C_6H_5N{=}C^{OH}\\C_6H_5N{=}C_{OH}\end{array}\right\rangle C\left\langle\begin{array}{l}OC_2H_5\\NHNHC_6H_5;\end{array}\right.$$

so that the reaction between the two substances taken has simply been a splitting off of one molecule of water. In order to convert the substance obtained into the hydrazone, it was heated at 115° to constant weight, which is attained after 10 hours.

0.1526 gram substance gave 0.3937 gram CO_2 and 0.0729 gram H_2O.

0.1532 gram substance gave 20.5 c.c. moist nitrogen at 16° and 745 mm.

	Theory for $C_{21}H_{18}N_4O_3$.	Found.
C	70.39	70.36
H	5.03	5.31
N	15.64	15.29

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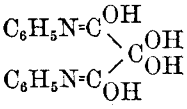
* Städeler, Ann. Chem. (Liebig), CVI. 253.

† V. Meyer and Dulk, Ann. Chem. (Liebig), CLXXI. 73.

The hydrazone, which is a yellow powder as obtained above, melts with decomposition at 163°; it dissolves rather easily in acetic acid, acetone, and benzine, but very slightly in alcohol and ether. It is insoluble in alkalies, and crystallizes from acetic acid in yellow leaflets. It does not take up water or alcohol again, which shows that in the above described hydrate and alcoholate these could not have been present in the form of crystal water.

Mesoxanilidehydrate = Dioxymalonic Anilide,



$$\begin{array}{l} C_6H_5N{=}C{<}^{OH}_{\ } \searrow C{<}^{OH}_{OH} \\ C_6H_5N{=}C{<}_{OH} \nearrow \end{array}$$

The crude mesoxanilidehydrate, which is directly obtained from mesoxanilidimidechloride and water, is best purified by dissolving in warm dilute sodic hydrate, reprecipitating with hydrochloric acid, and recrystallizing from water. It dissolves in boiling water in very slight amount (about one gram in a litre), and on cooling comes out in colorless needles, which do not change in weight on long standing over H_2SO_4 in vacuum. The crude hydrate can also be purified by recrystallization from warm (50°) alcohol; but in this case there is danger of a partial conversion into the alcoholate (see analysis I.). The pure alcoholate can, however, be completely converted back into the hydrate by dissolving it in sodic hydroxide, precipitating with acids, and recrystallizing from water (see analysis II.).

I. 0.1683 gram substance, recrystallized from alcohol (50°), and dried over H_2SO_4 in vacuum, gave 0.3961 gram CO_2 and 0.0753 gram H_2O.

II. 0.1565 gram substance, obtained from the alcoholate as above mentioned, gave 0.3604 gram CO_2 and 0.0711 gram H_2O.

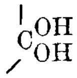
0.2508 gram substance gave 21.2 c.c. moist nitrogen at 17° and 763 mm.

	Theory for $C_{15}H_{14}N_2O_4$.	Found.	
		I.	II.
C	62.93	64.18	62.81
H	4.89	4.97	5.05
N	9.79	9.85	

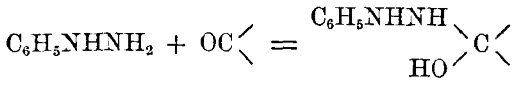
Mesoxanilidehydrate is soluble in benzine and acetic ether; the hot solutions are colored yellow, but in cooling become colorless, which shows that dissociation takes place on warming. On adding phenylhydrazine to a lukewarm solution of the hydrate in benzine, the hydrazon-hydrate already mentioned above separates out in white flakes. Mesoxanilidehydrate, heated in a capillary tube, behaves just like the corresponding alcoholate (see p. 119); heated at 100°, it loses one molecule of water very slowly, going over into yellow mesoxanilide. It requires about fifteen hours' heating at 100°–110°.

The most remarkable property of this substance is, however, its acid nature; it reddens blue litmus in aqueous solution, and dissolves without change in dilute sodic hydrate and carbonate.

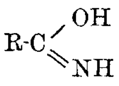
The fact that a substance containing the carbonyl group can attain acid properties by taking up one molecule of water,



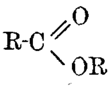
as well as the proof that phenylhydrazine simply adds itself in the first stage to a carbonyl group,



I regard as the most important result of the work on mesoxanilide. They will be fully discussed in connection with other observations at the end of this paper. I would like, however, to make here a few remarks concerning the constitution of the acid amides. It seems to me that the interesting experiments of Tafel and Enoch, in the case of benzamide,* and of Comstock and Kleeberg,† in the case of formanilide, have made it very probable that the acid amides possess the constitution represented by the formula



It follows that the product obtained by the action of ammonia on an acid ether,



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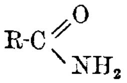
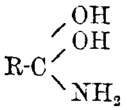
* Ber. d. chem. Ges., XXIII. 103 and 1550.

† American Chem. Journal, XII. 493.

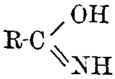
namely,



must take up water,



and then again split off water in a different way,



so that this reaction is not as simple as was formerly supposed.

The different behavior of the silver and sodium salt of an acid-amide seems to me to be cleared up by the work on acetacetic ether,* without the very improbable assumption that the salts are differently constituted, i. e. that tautomerism exists in this class of compounds.

Mesoxalic-acid-phenylhydrazone, from Mesoxanilidehydrate.

The proof that the above compounds are in reality derivatives of mesoxalic acid is the following.

Mesoxanilidehydrate was dissolved in four molecules pure sodic hydrate, and evaporated to dryness on a water bath. After taking up with water, and extracting with ether (to get rid of aniline split off), the aqueous solution was heated for 1½ hours longer, and then again evaporated to dryness.† After acidifying with dilute hydrochloric acid, whereby an evolution of carbon dioxide is noticed, and adding phenylhydrazine hydrochloride, a voluminous yellow precipitate results. It was purified by dissolving in dilute

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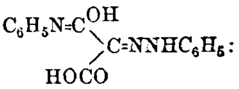
* Ann. Chem. (Liebig), CCLXVI. 135.

† It is necessary to heat so long because mesoxanilidehydrate goes over into mesoxalic acid with difficulty. In the first experiment the alkaline solution was evaporated only once on a water bath. On acidifying, and adding phenylhydrazine hydrochloride, a substance separated out in yellow needles, which, recrystallized from alcohol, melted with decomposition at 153°.

The analysis gave results agreeing well with an intermediate product,



	Theory.	Found.
C	63.60	63.17
H	4.59	4.62

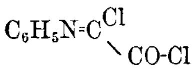
soda, acidifying, and washing the resulting yellow precipitate thoroughly.

0.1571 gram substance gave 0.2986 gram CO_2 and 0.0577 gram H_2O.

	Theory for $C_9H_8N_2O_4$.	Found.
C	51.92	51.83
H	3.85	4.08

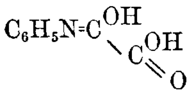
The substance melts between 158°–164° with decomposition, and is identical in every respect with a phenylhydrazone of mesoxalic acid, which Elbers first obtained from mesoxalic acid and phenylhydrazine, and which has since been obtained in other ways by R. Meyer * and v. Pechmann.†

That not a trace of oxanilchloride imidechloride,



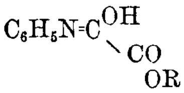
$$C_6H_5N{=}C\genfrac{}{}{0pt}{}{Cl}{CO{-}Cl}$$

is formed by the action of phosgene on phenylisocyanide, was proved as follows: the imidechloride just named must give on treatment with water oxanilic acid,



$$C_6H_5N{=}C\genfrac{}{}{0pt}{}{OH}{C\genfrac{}{}{0pt}{}{OH}{O}}$$

and of this substance not a trace could be found. In order to be absolutely certain, oxanilic acid was made by the method of Klinger, ‡ as well as that of Aschan, § and thus its properties known by actual experience. Incidentally it may be observed that on treating oxanilethane,



$$C_6H_5N{=}C\genfrac{}{}{0pt}{}{OH}{\genfrac{}{}{0pt}{}{CO}{OR}}$$

with alcoholic potash, according to the method of Klinger, ‡ a new unknown oxanilic acid was invariably obtained. It is readily soluble in hot water, but very difficultly soluble even in hot benzine; it crystallizes in needles, and does not melt at 210°. This is probably a polymeric modification, because in other respects the behavior is like that of oxanilic acid; it gives, for example, with

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[*] Ber. d. chem. Ges., XXIV. 1243.

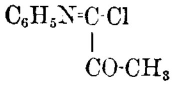
[†] Ibid., XXIV. 867.

[‡] Ann. Chem. (Liebig), CLXXXIV. 267.

[§] Ber. d. chem. Ges., XXIII. 1820.

phosphorus pentachloride (one molecule) Aschan's* oxanil-chloride melting at 82°, which, treated with water, gives the ordinary oxanilic acid, melting at 149°.

Pyruvic-anilidimidechloride,



$$\begin{array}{r} C_6H_5N{=}C{\cdot}Cl \\ | \quad\; \\ CO{\cdot}CH_3 \end{array}$$

If a mixture of 25 grams of phenylisocyanide and of freshly distilled acetylchloride be heated on a boiling water bath, in a few seconds so violent a reaction sets in that the entire mass carbonizes. The union of these substances can be accomplished quantitatively by taking a mixture of phenylisocyanide (10 grams) and acetylchloride (8.2 grams), and placing it first in lukewarm water, which is then gradually heated to the boiling point. The access of moist air is prevented by means of calcic chloride tubes, and the mixture shaken thoroughly, and, after the water once boils, heated only for about two minutes and then cooled quickly.

Several portions thus prepared are then united, and diluted with about five parts of absolute ether, whereby much or little polymerized phenylisocyanide separates out in brown voluminous flakes. After distilling off the ether from the filtrate, the dark brown residual oil is distilled under diminished pressure. A yellow oil was obtained, which distils with slight decomposition between 120°–125° at 20 mm. On redistilling, the chief portion came over at 136° at 30 mm., and gave the following results on analysis: —

0.2356 gram substance gave 0.5256 gram CO_2 and 0.1042 gram H_2O.

0.2463 gram substance gave 16.7 c.c. moist nitrogen at 17° and 747 mm.

0.1591 gram substance gave 0.1250 gram AgCl on ignition with CaO.

	Theory for C_9H_7NClO.	Found.
C	59.50	60.83
H	4.41	4.91
N	7.72	7.73
Cl	19.56	19.43

Pyruvic-anilidimidechloride is a yellow, very hygroscopic, sweet, and at the same time sharp-smelling oil, which, freshly made, does not contain a trace of phenylisocyanide. This is further shown by its behavior towards water, whereby pyruvic anilide,

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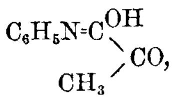
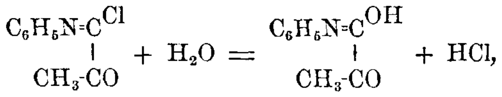
* Ber. d. chem. Ges., XXIII. 1823.



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \qquad\qquad \searrow \\ \qquad\qquad\quad CO, \\ \qquad CH_3 \nearrow \end{array}$$

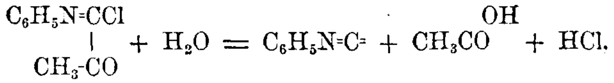
appears as the chief product, and no isonitrile is formed. The imidechloride is, however, an extremely unstable substance, and its preparation requires the greatest care; the phenylisocyanide used must be twice distilled at reduced pressure, and even then it may happen, especially if it is heated too long with the acetylchloride, that on attempting to distil under diminished pressure complete decomposition takes place. The imidechloride cannot be kept long, but decomposes on standing in a desiccator into phenylisocyanide and acetylchloride, the former substance at the same time undergoing marked polymerization. As shown below, the substance is decomposed by water into pyruvic anilide; on pouring it into a small quantity of alcohol, marked evolution of heat is noticed, and, on cooling, colorless leaflets of diphenylformamidine hydrochloride (mpt. 255°) separate out. The free base* obtained therefrom melts at 138°. This substance has such marked properties, and was obtained so often in the work on isonitriles, that an analysis was considered superfluous. The hydrochloride is especially characteristic; it dissolves in hot dilute hydrochloric acid, and crystallizes out almost completely on cooling (0°) in bulky hair-like needles, melting at 255°.

Very noteworthy is the totally different behavior of the imidechloride towards water and alkalies; for whereas it reacts with the former, giving pyruvic anilide, according to the equation,



$$\begin{array}{c} C_6H_5N{=}C^{Cl} \\ | \\ CH_3\text{-}CO \end{array} + H_2O = \begin{array}{c} C_6H_5N{=}C^{OH} \\ | \\ CH_3\text{-}CO \end{array} + HCl,$$

it is split on pouring into dilute sodic hydrate, chiefly into the components, as follows:



$$\begin{array}{c} C_6H_5N{=}CCl \\ | \\ CH_3\text{-}CO \end{array} + H_2O = C_6H_5N{=}C{=} + \overset{OH}{CH_3CO} + HCl.$$

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* Hofmann, Jahresber. 1858, p. 354.

16 grams of pyruvic-anilidimidechloride, for example, were divided into two parts, and treated simultaneously as follows.

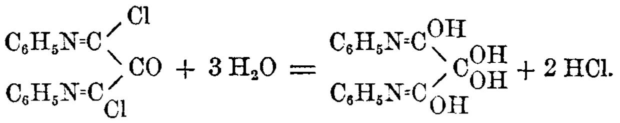
a. 8.3 grams were slowly poured into 200 c.c. of sodic hydrate (1:10), which was kept at 0° by means of ice. A strong smell of isonitrile is noticed immediately. After standing for an hour, during which the mass was kept well stirred, it was extracted with ether. The ether was then distilled off, and the residue distilled with steam, the distillate thereupon extracted with ether, and, in order to remove any aniline possibly formed, treated with dilute sulphuric acid. After drying the ether solution with solid caustic potash, there was left, after getting rid of the ether, 2.4 grams of oil, which was practically pure phenylisocyanide.

b. 7.7 grams poured slowly into 110 c.c. of ice water solidified quickly, and not a trace of phenylisocyanide was noticed. From the solid mass 4 grams of pure pyruvic anilide (see below), were obtained.

The same noteworthy difference in behavior towards water and alkalies is also shown by mesoxanilidimidechloride (described above). Whereas water converts it into mesoxanilidehydrate, and not a trace of phenylisocyanide is observed, on pouring the substance into dilute sodic hydrate (1:10), very much phenylisocyanide results. In an experiment carried out as above under *a*, 1 gram isonitrile was obtained from 4 grams of imidechloride.

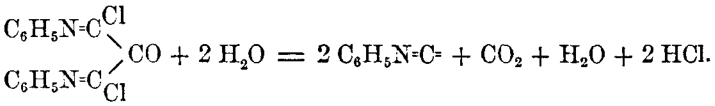
This substance is therefore also split in two ways, according to the conditions: —

1. With water,



$$\left.\begin{array}{l}C_6H_5N{=}C^{Cl}\\ C_6H_5N{=}C_{Cl}\end{array}\right\rangle CO + 3\,H_2O = \left.\begin{array}{l}C_6H_5N{=}C^{OH}\\ C_6H_5N{=}C_{OH}\end{array}\right\rangle C\begin{array}{l}OH\\ OH\end{array} + 2\,HCl.$$

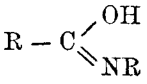
2. With alkalies,



$$\left.\begin{array}{l}C_6H_5N{=}C^{Cl}\\ C_6H_5N{=}C_{Cl}\end{array}\right\rangle CO + 2\,H_2O = 2\,C_6H_5N{=}C{=} + CO_2 + H_2O + 2\,HCl.$$

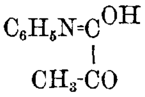
This is, however, not at all a behavior peculiar to the two cases mentioned, but seems to be a very general property of imidechlorides. Wallach and his co-workers * have often noticed, in their work on this class of substances, that on pouring amide and imide chlorides into sodic hydrate, a strong smell of isonitrile appeared. The amount formed was never determined, and they were unable to offer an explanation for its formation; its appearance was supposed to be due to the presence of some unknown impurity.

The above results make it probable that a new method for making isonitriles is accessible through the alkylated acid amides,



and phosphorus pentachloride. Up to the present time, however, no further experiments have been carried out in this direction.

Pyruvic Anilide,



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \quad\;\; | \\ CH_3{-}CO \end{array}$$

In order to prepare this substance, it is not necessary to start with pure distilled pyruvic-anilidimidechloride. The crude product obtained by heating phenylisocyanide and acetylchloride is poured into a large amount of water, and in a short time the oil solidifies, with marked evolution of heat. The mass is ground to a fine powder, filtered off, and then crystallized once from boiling water. Recrystallized once more from alcohol, a perfectly colorless product is obtained, melting at 104°. The yield equals generally in weight that of the isonitrile applied.

0.1697 gram substance dried over H_2SO_4 in vacuum gave 0.4120 gram CO_2 and 0.0854 gram H_2O.

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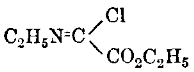
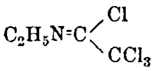
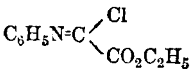
* Wallach, Ann. Chem. (Liebig), CLXXXIV. 75 and 75; in the case of



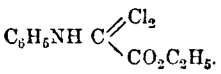
Wallach, Ann. Chem. (Liebig), CCXIV. 226; in the case of



Klinger, Ann. Chem. (Liebig), CLXXXIV. 270, 276, 279, and 283; in the case of



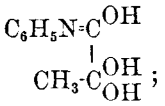
and



0.2739 gram substance dried over H_2SO_4 in vacuum gave 20.8 c.c. moist nitrogen at 24° and 756 mm.

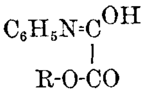
	ory for $C_9H_9NO_2$.	Found.
C	66.25	66.15
H	5.52	5.59
N	8.59	8.47

Pyruvic anilide dissolves in large amount in hot, but very little in cold alcohol. It is insoluble in cold water, and about 7 grams dissolve in a litre of boiling water. It crystallizes in long colorless needles, and is also soluble in chloroform and ether (in the latter case not easily). The substance is very stable towards warm dilute hydrochloric and sulphuric acids, and long boiling therewith causes little change. Caustic alkalies, as well as ammonia, act upon it immediately; although insoluble in sodic carbonate, and giving no reaction to test paper, pyruvic anilide dissolves in the cold in two molecules dilute sodic hydrate. On acidifying, however, not the original substance is obtained, but a product comes down in white flakes melting at 196°. This is in all probability a polymeric pyruvic anilide, and the reaction which takes place is the following. At first, the pyruvic anilide, just as the mesoxanilide above, takes up a molecule of water, forming the hydrate



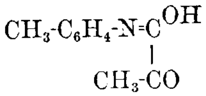
$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \qquad\quad | \\ \quad CH_3{-}C^{OH}_{OH} \end{array} ;$$

on acidifying, it loses water, and simultaneously with this, polymerization results. This becomes especially probable on comparing the entirely similar behavior towards alkalies of oxanilethane (page 125),



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \qquad\quad | \\ \quad R{-}O{-}CO \end{array}$$

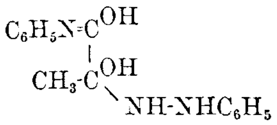
and of pyruvic-*o*-toluide (page 145),



$$\begin{array}{l} CH_3{-}C_6H_4{-}N{=}C^{OH} \\ \qquad\qquad\qquad | \\ \qquad\quad\ \ CH_3{-}CO \end{array}$$

Attempts to split pyruvic anilide into pyruvic acid (in alkaline solutions) were unsuccessful, although in every case almost the calculated amount of aniline was obtained. The conversion into pyruvic acid was accomplished finally in a roundabout way, namely, by means of phenylhydrazine.

Pyruvic-anilide-phenylhydrazonehydrate,



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \quad | \\ CH_3{-}C^{OH}_{\diagdown NH{-}NHC_6H_5} \end{array}$$

On adding to a cold ethereal solution of pyruvic anilide one molecule of phenylhydrazine, a voluminous white precipitate separates out almost immediately in the form of needles. After filtering off, washing well with ether, and drying a short time over sulphuric acid in a vacuum, a perfectly pure preparation is obtained.

I. 0.1522 gram substance gave 0.3738 gram CO_2 and 0.0896 gram H_2O.

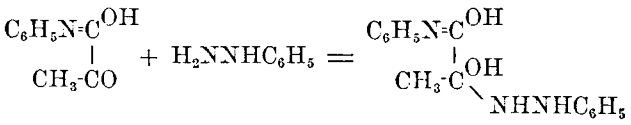
II. 0.1512 gram substance gave 0.3688 gram CO_2 and 0.0907 gram H_2O.

I. 0.1516 gram substance gave 21 c.c. moist nitrogen at 18° and 748 mm.

II. 0.1506 gram substance gave 20.5 c.c. moist nitrogen at 18° and 744 mm.

	Theory for $C_{15}H_{17}N_3O_2$.	Found. I.	Found. II.
C	66.40	66.98	66.52
H	6.30	6.54	6.66
N	15.50	15.74	15.38

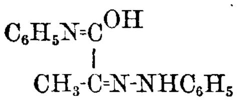
Phenylhydrazine has thus simply added itself to pyruvic anilide, just as in the case of mesoxanilide, as follows:



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \quad | \\ CH_3{-}CO \end{array} + H_2NNHC_6H_5 = \begin{array}{l} C_6H_5N{=}C^{OH} \\ \quad | \\ CH_3{-}C^{OH}_{\diagdown NHNHC_6H_5} \end{array}$$

That the resulting substance is not a salt-like compound, but an addition product, is certain, since alkalies do not split it into its components. The hydrazonehydrate thus obtained loses on long standing, or quickly at 70°, water going over into the hydrazone. Heated quickly in a capillary tube it melts with gas evolution (water) between 101°–105°, and then solidifies again, and melts on further heating at about 160°.

Pyruvic-anilide-phenylhydrazone,



$$\begin{array}{l} C_6H_5N{=}C^{OH} \\ \qquad\quad | \\ CH_3{-}C{=}N{-}NHC_6H_5 \end{array}$$

If the above hydrazone-hydrate be heated a short time in alcoholic or in acetic acid solution, or pyruvic anilide be treated in hot alcoholic solution with one molecule of phenylhydrazine, the phenylhydrazone of pyruvic anilide is formed quantitatively. Recrystallized twice from alcohol, it is obtained in colorless needles, melting at 176°, and after drying at 110° it gave the following results on analysis: —

0.1508 gram substance gave 0.3930 gram CO_2 and 0.0819 gram H_2O.

0.1736 gram substance gave 25.6 c.c. moist nitrogen at 17° and 734 mm.

	Theory for $C_{15}H_{15}N_3O$.	Found.
C	71.14	71.07
H	5.93	6.03
N	16.60	16.52

The hydrazone is easily soluble in hot benzine, alcohol, and acetic acid, and comes out on cooling in colorless needles. It is insoluble in alkalies or in dilute acids.

Phenylhydrazone of Pyruvic Acid, from Pyruvic Anilide.

The proof that the above compounds are in reality derivatives of pyruvic acid is as follows. 3.5 grams pyruvic-anilidephenylhydrazonehydrate were treated with 120 c.c. sodic hydrate (1:10), and heated in an open dish on a water bath for half an hour. The formation of aniline was recognized by the smell, chloride of lime reaction, and by conversion into acetanilide. After cooling and filtering, the solution is acidified with dilute hydrochloric acid. A very bulky precipitate, consisting of yellow needles (2 grams) was obtained. It was dissolved in soda, reprecipitated by acids, and finally recrystallized from alcohol. The product obtained melted with decomposition at 192°, and was identical in every particular with a preparation which was made according to the directions of E. Fischer and Jourdan.*

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* Ber. d. chem. Ges., XVI. 224, XVII. 578.

0.2018 gram substance dried over H_2SO_4 in a vacuum gave 0.4515 gram CO_2 and 0.1061 gram H_2O.
0.1495 gram substance dried over H_2SO_4 in a vacuum gave 20.8 c.c. moist nitrogen at 17° and 748 mm.

	Theory for $C_9H_{10}N_2O_2$.	Found.
C	60.68	61.01
H	5.62	5.84
N	15.73	15.88

Hydrochloride of Phenylimidoformylchloride, $2\,C_6H_5N{=}C^{H}_{Cl}$, HCl.

On passing hydrochloric acid gas, which has been dried by means of phosphorus pentoxide, over phenylisocyanide, cooled to —15°, so violent a reaction takes place that it is not possible to regulate it, even by diluting the gas with dry carbon dioxide. The addition of hydrogen chloride to the isonitrile can however be accomplished quantitatively, if the latter be diluted with 6 to 8 times its volume of absolute ether, and the *dry* gas be passed over this solution, cooled to —15°, until it smells of hydrogen chloride; a white powder separates out, soon after the above operation is begun, and after it is ended the mixture is allowed to stand fifteen minutes. An equal volume of *dry* ligroine (bpt. 70°-80°) is then added, the white precipitate is washed by decantation, and spread out on porous clay plates, and transferred as quickly as possible to a desiccator. After twelve hours' standing in a vacuum, it was perfectly dry, and gave the following results on analysis: —

0.2193 gram substance gave 0.2939 gram AgCl (Carius).
0.2024 gram substance gave 0.2681 gram AgCl (Carius).
0.2875 gram substance gave 22 c.c. moist nitrogen at 20° and 750 mm.

	Theory for $C_{12}H_{13}N_2Cl_3$.	Found. I.	II.
Cl	33.75	33.11	32.77
N	8.87	8.64	

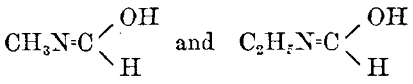
That a salt of the formula $2\,C_6H_5N{=}C{=}$, 3 HCl, is formed, is proved with greater precision even than by the analysis by the following experiment. 20 grams phenylisocyanide treated as described with hydrogen chloride, etc., gave 30.8 grams pure dry salt (calculated 30.6 grams). The salt thus obtained is a colorless powder, which cannot be kept very long without decomposition; it is very hygroscopic, has a strong acid smell like an acid haloid, and is instantly decomposed by water or alcohol with marked evolution of heat. The salt dissolves in chloroform, but is insoluble in ether and ligroine. Its behavior towards water and alkalies was carefully studied. 16 grams were added slowly to 300 c.c. sodic hydrate (1:10) kept at 0° by means of ice. Reaction instantly takes place, and a portion goes into solution, another remains as a sticky grayish mass. The mixture is immediately extracted with ether, and, to get rid of any diphenylformamidine taken up by the ether, washed with dilute hydrochloric acid. The ethereal solution is then washed with soda, and dried with calcic chloride. After distilling off the ether, 3 grams of an oily residue were obtained, consisting chiefly of formanilide. On adding ligroine and cooling, the formanilide solidified (2 grams), and recrystallized from a mixture of ligroine and ether was obtained pure (mpt. 48°).

The above mentioned hydrochloric acid extract, as well as some residue not extracted by the ether in the first place, contains diphenylformamidine (mpt. 138°). 1.5 grams were obtained.

In an experiment where 15.8 grams phenylimidoformylchloride salt and 180 c.c. of water were taken, and the experiment otherwise carried out as above with sodic hydrate, 2 grams of formanilide and .4 gram diphenylformamidine were obtained.

The formation of diphenylformamidine in the two cases above is easily explained by considering that aniline is split off; and, in fact, the presence of aniline, as well as that of formic acid, in both reactions was proved.

Gautier * also obtained, by treating methyl- and ethylisocyanide with dry hydrogen chloride, salt-like products of the general formula $2\,RNC, 3\,HCl$. He further found that they are instantly decomposed by water and caustic potash, giving methyl- and ethylformiamide respectively



$$CH_3N{=}C\begin{smallmatrix}OH\\H\end{smallmatrix} \quad \text{and} \quad C_2H_5N{=}C\begin{smallmatrix}OH\\H\end{smallmatrix}$$

as chief products.

These experiments are sufficient to prove that the isonitriles react with hydrogen chloride giving hydrochlorides of alkylimideformylchlorides,

$$2\,RN{=}C^{H}_{Cl},\ HCl.$$

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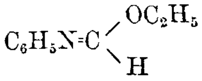
* *Loc. cit.*, XVII. 223 and 240.

On passing dry hydrogen chloride into a chloroform or an ethereal solution of phenylisocyanide (cooled to —15°) to which exactly one molecule of alcohol has been added,[*] there is formed diphenylformamidinehydrochloride, and not a trace of phenylformimidoether,



$$C_6H_5N{=}C\begin{matrix}\diagup OC_2H_5\\ \diagdown H\end{matrix}$$ [†]

The same result is obtained on treating an alcoholic solution of phenylisocyanide (5 grams) with a few drops of alcoholic hydrogen chloride.

Prussic acid reacts likewise with halogen hydrides, forming white salt-like products. Thus Claisen and Matthews [‡] have obtained, by using acetic ether as a diluter, the salts 2 HNC, 3 HCl, and 2 HNC, 3 HBr.

With regard to the nature of the products formed by directly passing dry hydrogen haloids into anhydrous prussic acid, there is no accord in the literature, especially in the case of the product obtained with hydriodic acid. The last named substance was discovered almost simultaneously by Gal [§] and by Gautier,[‖] and the formula HNC,HI confirmed by both by means of analyses.

The description of the products obtained is however entirely different. Gal, on the one hand, describes his product as crystallizing in wart-like aggregates, which are instantly decomposed by water; whereas Gautier, on the other hand, states that his substance crystallizes in rhombohedra, has a refreshing salty but not acid taste; it is very soluble in water and in alcohol, with neutral reaction to test paper, and crystallizes from the latter solvent without decomposition. The substance is not hygroscopic, and sublimes without melting at 350°–400°.

These are, however, pretty exactly the properties of ammonium iodide; hence it follows that Gautier's supposed prussic acid salt was nothing else than ammonium iodide. This becomes the more probable because of the fact that Gautier, in his last paper [¶] on prussic acid, describes an addition product, HNC,HI, of entirely different properties, without correcting his previous statements or drawing attention to the difference. The results obtained in that paper agree entirely with Gal's previous statements.

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[*] Pinner, Ber. d. chem. Ges., XVI. 354, 1644.

[†] Comstock and Clapp, Amer. Chem. Jour., XIII. 527.

[‡] Ber. d. chem. Ges., XVI. 310.

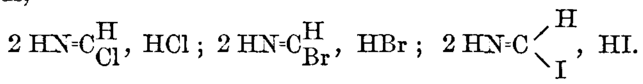
[§] Comptes Rendus, LXI. 643.

[‖] Bull. de la Soc. Chim., IV. 88; Comptes Rendus, LXI. 380.

[¶] *Loc. cit.*, XVII. 143.

I have, therefore, also made this salt in large amounts from pure prussic acid (bpt. 26°.2) and hydriodic acid, dried by means of phosphorus pentoxide, and can confirm Gautier's detailed statements in Annales de Chimie et de Physique, [4.], XVII. 143, in every respect. The substance is extremely unstable, and can only be dried about a minute over sulphuric acid in vacuum; in ten minutes such marked decomposition takes place that no analysis of it can be carried out.

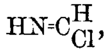
From the results obtained above in the case of the isonitriles, and from the experiments of Claisen and Matthews, it becomes very probable that all the salt-like products obtained from prussic acid and the halogen hydrides are constituted according to the general formula, 2 HNC, 3 HX. These compounds are, as Claisen and Matthews* already regard as probable, salts of imidoformyl haloids,



$$2\,HN{=}C^{H}_{Cl},\ HCl;\quad 2\,HN{=}C^{H}_{Br},\ HBr;\quad 2\,HN{=}C\begin{smallmatrix}\diagup H\\ \diagdown I\end{smallmatrix},\ HI.$$

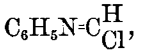
Gautier has already shown in his last paper† that hydrobromic acid forms with prussic acid a salt of the formula 2 HNC, 3 HBr. He thereby corrects his previous statements, as well as those of Gal. It is, therefore, highly probable that the salts HNC, HCl, and HNC, HI, analyzed formerly, may have contained mechanically enclosed prussic acid, since the substances were only dried a few seconds over sulphuric acid in a vacuum.

Furthermore, some new observations have been made which make it improbable that imidoformylchloride,



$$HN{=}C^{H}_{Cl},$$

and phenylimidoformylchloride,



$$C_6H_5N{=}C^{H}_{Cl},$$

are capable of existence. It is to be expected that these substances should be volatile liquids. On treating potassic formiate with 2 molecules of phosphorus oxychloride, or with 3 molecules of phosphorus trichloride, a violent reaction sets in at 0°, and a mixture of carbonic oxide and hydrochloric acid results, which shows that the formylchloride,

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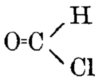
* Ber. d. chem. Ges., XVI. 311.

† *Loc. cit.*, XVII. 141.



$$O{=}C\begin{matrix}H\\Cl\end{matrix}$$

first formed decomposes spontaneously.

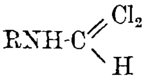
On treating aniline potassium, $C_6H_5NK_2$, (which is obtained as a dark brown hygroscopic powder, on adding potassium to an excess of aniline, and then heating the mixture in an atmosphere of hydrogen, first in order to dissolve the potassium, and finally to get rid of the aniline, to a temperature of 310°,) with 1 molecule of chloroform, a violent reaction takes place in the cold, but the resulting product is not phenylimidoformylchloride,

$$C_6H_5NK_2 + CHCl_3 = C_6H_5N{=}C^{H}_{Cl},$$

but its decomposition products, phenylisocyanide and hydrochloric acid. The last named substance then unites with part of the isonitrile set free to form the salt,

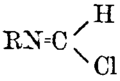
$$2\,C_6H_5N{=}C^{H}_{Cl},\ HCl.$$

The above observations are sufficient to clear up fully the reaction which takes place on treating a primary amine with chloroform and caustic potash.* The amine RNH_2 forms at first with the caustic potash present a mono- and a di-potassium salt, $RNHK$ and RNK_2. These salts then react with the chloroform, giving rise to the amide and imidechlorides,



$$RNH\text{-}C\begin{matrix}Cl_2\\H\end{matrix}$$

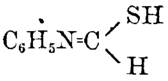
and



$$RN{=}C\begin{matrix}H\\Cl\end{matrix}$$

which are then converted by the caustic potash present into potassic chloride and alkylisocyanide.

This noteworthy tendency to split off hydrogen and another univalent group (here chlorine) from one and the same carbon atom is not limited to the cases observed above. It is also, as is known, a property of thioformanilide,†



$$C_6H_5N{=}C\begin{matrix}SH\\H\end{matrix}$$

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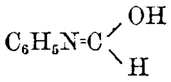
[*] A. W. Hofmann, Ann. Chem. (Liebig), CXLIV. 116.

[†] A. W. Hofmann, Ber. d. chem. Ges., X. 1097.

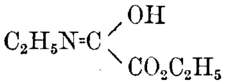
and, to a slight degree, as I have found, of formanilide,



$$C_6H_5N{=}C\Big\langle\begin{matrix}OH\\H\end{matrix}$$

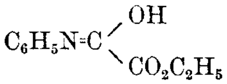
on distillation. In these two cases, however, notwithstanding many experiments, it was found impossible to attain a quantitative splitting off of H_2S or H_2O respectively, because at higher temperature the isonitriles polymerize to a marked extent.

A decomposition in the same direction has also been observed by Wallach,* on distilling



$$C_2H_5N{=}C\Big\langle\begin{matrix}OH\\CO_2C_2H_5\end{matrix}$$

and by Klinger,† on distilling oxanilethane,



$$C_6H_5N{=}C\Big\langle\begin{matrix}OH\\CO_2C_2H_5\end{matrix}$$

The formation of isonitriles and their polymeric products (resins) in the above cases shows how strong a tendency exists for the splitting off in this direction. This same thing is to be seen in the decompositions described above under pyruvic-anilidimidechloride (pp. 127 and 128).

II. On *o*-Tolylisocyanide, $CH_3{-}C_6H_4N{=}C{=}$.

Preparation of o-Tolylisocyanide. — 210 grams of caustic potash are dissolved in about 800 c.c. alcohol (99%), and a mixture of 190 grams chloroform and 100 grams *o*-toluidine added slowly, following in other respects the directions given under phenylisocyanide.

Whereas, in the case of aniline only about 15 grams pure phenylisocyanide are obtained from 100 grams of the amine taken, here at least 25 grams pure *o*-tolylisocyanide always result.

o-Tolylisocyanide boils constant and without leaving any residue at 75° at 16 mm., and at 101° at 55 mm. pressure: it boils with but slight decomposition at 183°–184° (thermometer entirely in the vapor) at ordinary pressure (753 mm.). It is a colorless oil, its specific gravity being 0.968 at 24° (Westphal): on standing, the oil becomes colored pale greenish yellow. As regards smell and physiological action, it closely resembles phenylisocyanide. It is far more stable, however, than the lower homologue, and shows little tendency to polymerize, even at 180°, and can therefore be kept a long time without much change, except that the color changes to dark yellow. The substance is readily volatile with steam.

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* Ann. Chem. (Liebig), CLXXXIV. 60.

† Ann. Chem. (Liebig), CLXXXIV. 265.

0.1454 gram substance gave 0.4370 gram CO_2 and 0.0807 gram H_2O.

0.2499 gram substance gave 26.5 c.c. moist nitrogen at 22° and 756 mm.

	Theory for C_8H_7N.	Found.
C	82.05	81.97
H	5.98	6.17
N	11.97	11.95

Behavior towards Organic Acids. — On pouring 18 grams *o*-tolylisocyanide into 2 molecules pure formic acid, cooled to 0°, a violent reaction sets in with evolution of pure carbonic oxide. The residue consists of form-*o*-toluide, which boils at 286°, and crystallizes from a mixture of ligroine and ether in six and eight sided leaflets, melting at 62°. It is identical in every respect with a form-*o*-toluide obtained directly from *o*-toluidine and formic acid according to Ladenburg's direction.*

0.1744 gram substance gave 0.4567 gram CO_2 and 0.1060 gram H_2O.

0.2044 gram substance gave 18.2 c.c. moist nitrogen at 15° and 752 mm.

	Theory for C_8H_9NO.	Found.
C	71.11	71.41
H	6.66	6.75
N	10.37	10.32

On mixing *o*-tolylisocyanide with 2 molecules of acetic acid reaction sets in on warming gently: there is formed, after distilling under reduced pressure, acetic anhydride and a mixture of form-*o*-toluide and acet-*o*-toluide † (mpt. 108°). Towards anhydrous oxalic acid *o*-tolylisocyanide behaves exactly like phenylisocyanide. On heating *o*-tolylisocyanide with benzoic acid reaction takes place in an entirely analogous manner, and on distilling benz-*o*-toluide (mpt. 142°) is obtained as the chief product.

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* Ber. d. chem. Ges., X. 1129. He gives the melting point, 56.°5–57.°5.

† Lehmann, Jahresber. 1882, p. 369. Beilstein, Kühlberg, Ann. Chem. (Liebig), CLVI. 77.

Molecular Rearrangement. — The conversion of *o*-tolylisocyanide into *o*-tolylcyanide [*] takes place quantitatively on heating 4 c.c. of the former in a sealed tube for three hours at 235°–245° (at 180°–200° no change whatever takes place). 3 grams of *o*-tolylcyanide were obtained, boiling at 202°–203° (thermometer entirely in the vapor) at 728 mm.; and from this, by saponification with sulphuric acid, [†] *o*-toluylic acid melting at 104°.

This molecular rearrangement has already been noticed by Weith, [‡] in the case of an *o*-tolylisocyanide containing *o*-toluidine. Weith was in fact the first to prove that the alkylisocyanides, RNC, go over by molecular rearrangement into the corresponding alkylcyanides, RCN. Gautier states, in a preliminary paper, [§] that the boiling point of methyl and ethylisocyanide is raised after some standing, and thinks that this is to be explained by a partial conversion into methyl and ethylcyanide. In his last paper [‖] on the isonitriles he says nothing whatever about this supposed molecular rearrangement, but states that on long heating of methyl and ethylisocyanide in sealed tubes at 200°, a portion polymerizes, but that much unchanged isonitrile is left. A molecular rearrangement in the case of the isonitriles has therefore only been proved in the case of phenyl- and of *o*-tolylisocyanide. [¶]

Action of Primary Amines. — 4 grams *o*-tolylisocyanide were heated with reversed condenser with 4.4 grams *o*-toluidine for forty minutes at 190°–220°. On cooling, no isonitrile smell was left, and the dark brown solid residue was recrystallized four times from alcohol; thus 2.2 grams perfectly pure *o*-ditolylformamidine, [**] melting point 151°, were obtained.

0.2033 gram substance, dried at 110°, gave 22.5 c.c. moist nitrogen at 16° and 748 mm.

	Theory for $C_{15}H_{16}N_2$.	Found.
N	12.50	12.69

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[*] Cf. Weith, Ber. d. chem. Ges., VII. 722.

[†] Cahn, Ann. Chem. (Liebig), CCXL. 280.

[‡] Ber. d. chem. Ges., VII. 722.

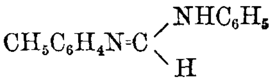
[§] Comptes Rendus, LXV. 862; Ann. Chem. (Liebig), CXLVI. 128.

[‖] *Loc. cit.*, XVII. 226.

[¶] Compare the discussion of Weith and Hofmann on this subject in Ber. d. chem. Ges., VII. 722, 814, 1017, 1021.

[**] Ladenburg, Ber. d. chem. Ges., X. 1260.

If 10 grams of *o*-tolylisocyanide be heated with 1½ molecules of aniline for twenty-five minutes at 190°–220°, the reaction is completed, and no isonitrile left. In this case, however, not only phenyl-*o*-tolylformamidine,

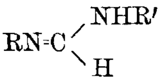


$$CH_5C_6H_4N{=}C\begin{array}{l}\diagup NHC_6H_5\\ \diagdown H\end{array}$$

results, but a mixture from which I succeeded only in separating out diphenylformamidine as a pure product.

A similar result is obtained on heating 10 grams phenylisocyanide with 10.5 grams *o*-toluidine for two hours at 190°–220°: from the resulting mixture of amidine products, 0.4 gram of pure *o*-ditolylformamidine (melting point 151°) could be isolated with ease.

These experiments show that the addition of primary amines takes place somewhat more readily in the case of *o*-tolylisocyanide than with phenylisocyanide; and further, that the resulting dialkylated formamidine derivatives,



$$RN{=}C\begin{array}{l}\diagup NHR'\\ \diagdown H\end{array}$$

are homogeneous only when the two alkyl groups (R and R′) are the same.

Action of Sulphur.— 5 grams *o*-tolylisocyanide and the calculated amount of crystallized sulphur, in the presence of carbon bisulphide, were heated in a sealed tube for two hours at 130°. No isonitrile was left, and after distilling off the carbon bisulphide, the residue was distilled with steam. The mustard oil thus carried over, after extracting with ether and drying with calcic chloride, boiled, on fractionating, at 236°–237° (thermometer entirely in the vapor) at 726 mm. It was identical in all its properties with *o*-tolyl mustard oil,* $CH_3{-}C_6H_4{-}N{=}C{=}S$, and gave the following result on a sulphur determination:

0.2681 gram substance gave 0.4064 gram $BaSO_4$ (Carius).

	Theory for C_8H_7NS.	Found.
S	21.47	20.81

Action of Hydrogen Sulphide. — An alcoholic solution of *o*-tolylisocyanide was saturated at 0° with sulphuretted hydrogen, and then heated in a sealed tube for four hours at 100°. The hydrogen sulphide had completely disappeared, and, after distilling off the alcohol, the residue was taken up with ether and shaken with sodic hydrate. On acidifying the alkaline solution, thioform-*o*-toluide separates out in yellow, bulky flakes; recrystallized three times from ligroine (bpt. 70°–80°), using animal charcoal, it is obtained in perfectly colorless needles, melting at 100°–101°. Senier* describes thioform-*o*-toluide as a yellow substance, melting at 94°–96° (crystallized from alcohol).

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* Girard, Ber. d. chem. Ges., VI. 445.

0.1986 gram substance, dried at 70°–80°, gave 0.2928 gram $BaSO_4$ (Carius).

	Theory for C_8H_9NS.	Found.
S	21.19	20.29

Isocyan-o-tolylchloride or o-Tolylimidocarbonylchloride, $CH_3\text{-}C_6H_4N\text{=}C\text{=}Cl_2$.

This substance is formed quantitatively on passing dry chlorine into a chloroform solution of *o*-tolylisocyanide, as above in the case of isocyanphenylchloride. As soon as the presence of unabsorbed chlorine can be detected, the reaction is ended, and the solution immediately washed with dilute sodic hydrate, and dried with calcic chloride. On fractionating, a colorless sharp-smelling oil is obtained, which boils at 214°–215° (uncorr.).

0.1384 gram substance gave 0.2593 gram CO_2 and 0.0520 gram H_2O.

0.2230 gram substance gave 15 c.c. moist nitrogen at 23° and 756 mm.

0.2103 gram substance gave 0.3201 gram AgCl (Carius).

	Theory for $C_8H_7NCl_2$.	Found.
C	51.06	51.09
H	3.73	4.17
N	7.45	7.54
Cl	37.76	37.65

o-Toluidine converts the isocyan-*o*-tolylchloride quantitatively into *o*-tritolylguanidine hydrochloride. In order to isolate the free base, the solution is made slightly alkaline, and the excess of toluidine got rid of by distilling with steam. The residue, recrystallized twice from alcohol, gave flat needles of *o*-tritolylguanidine,

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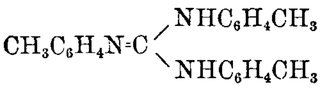
* Ber. d. chem. Ges., XVIII 2293.

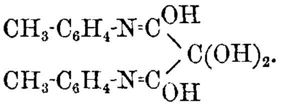


$$CH_3C_6H_4N{=}C\begin{cases}NHC_6H_4CH_3\\NHC_6H_4CH_3\end{cases}$$

melting point, 131°.*

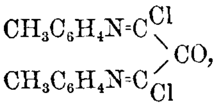
Lachmann † has described a substance as isocyan-*o*-tolylchloride, which he obtained by treating *o*-tolylmustard oil with chlorine, according to the directions of Sell and Zierold. He studied it but little, and gives the boiling point 218°, whereas the above product boils at 214°–215°. That Lachmann's product was not a homogeneous substance follows from the facts given above under isocyanphenylchloride (p. 115).

Mesox-o-toluidehydrate = Dioxymalonic-o-toluide,



$$\begin{matrix}CH_3\text{-}C_6H_4\text{-}N{=}C^{OH}\\CH_3\text{-}C_6H_4\text{-}N{=}C_{OH}\end{matrix}\Big>C(OH)_2.$$

Phosgene reacts on *o*-tolylisocyanide energetically below 0°. The union of these substances was accomplished as above in the case of phenylisocyanide. In this instance, however, no attempt was made to purify the resulting yellow imidechloride,



$$\begin{matrix}CH_3C_6H_4N{=}C^{Cl}\\CH_3C_6H_4N{=}C_{Cl}\end{matrix}\Big>CO,$$

by distillation. The crude product, after the excess of phosgene had been removed by heating on a water bath, was directly poured into a large amount of water: in a short time, the imidechloride is converted into mesox-*o*-toluidehydrate and hydrochloric acid, with marked evolution of heat. The crude solid mass was first recrystallized from benzine, and then dissolved in sodic hydrate, precipitated again by acids, and finally recrystallized from much hot water.

0.1530 gram substance, dried over H_2SO_4 in vacuum, gave 0.3641 gram CO_2 and 0.0812 gram H_2O.

0.1920 gram substance gave 14.6 c.c. moist nitrogen at 16° and 762 mm.

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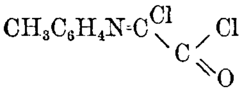
* Berger, Ber. d. chem. Ges., XII. 1857.

† Ber. d. chem. Ges., XII. 1349. He does not state whether an analysis of the product obtained was carried out.

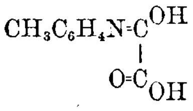
	Theory for $C_{17}H_{18}N_2O_4$.	Found.
C	64.97	64.90
H	5.73	5.90
N	8.88	8.89

Mesox-*o*-toluidehydrate resembles in every particular the above described mesoxanilidehydrate. It is an acid, which reddens blue litmus paper, and dissolves in dilute sodic carbonate. Heated quickly in a capillary tube it becomes yellow at 100°, and melts with gas evolution (water) at 127°–131°. About two grams dissolve in a litre of boiling water, and, on cooling, the greater portion comes out again in colorless needles. It dissolves in hot anhydrous benzine with yellow color, which shows that dissociation takes place, because on cooling (to 50°) the solution becomes colorless. The substance, crystallizing out from hot benzine, on cooling, never consists entirely of mesox-*o*-toluidehydrate, but contains mesox-*o*-toluide as an analysis proved.

That no oxal-*o*-toluidechloride imidechloride,

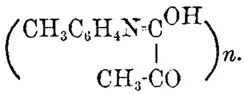


is formed by the action of phosgene on *o*-tolylisocyanide is extremely probable, since, on decomposing the imidechloride obtained, with water not a trace of oxal-*o*-toluidic acid,



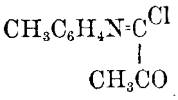
$$\begin{array}{l} CH_3C_6H_4N{=}C^{OH} \\ \qquad\qquad\quad | \\ \qquad\qquad O{=}C_{OH} \end{array}$$

was obtained.*

π-Pyruvic-o-toluide, 

$$\left(\begin{array}{l} CH_3C_6H_4N{=}C^{OH} \\ \qquad\qquad\quad | \\ \qquad\quad CH_3{-}CO \end{array}\right)n.$$

o-Tolylisocyanide and freshly distilled acetylchloride (one molecule) unite quantitatively, after five minutes' heating on a water bath. The resulting yellow-colored imidechloride,



$$\begin{array}{l} CH_3C_6H_4N{=}C^{Cl} \\ \qquad\qquad\quad | \\ \qquad\quad CH_3CO \end{array}$$

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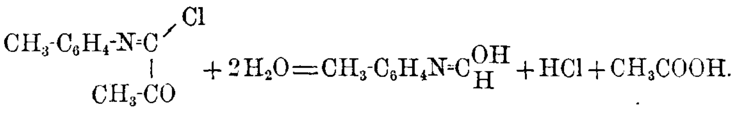
* Mauthner and Suida, Monatshefte für Chemie, VII. 234.

is in this case very unstable, and cannot be distilled under reduced pressure, but dissociates to a marked extent into the constituents.

On pouring the crude product (18 grams) into 130 c.c. of water, cooling with running water, it becomes solid very soon. In this case form-*o*-toluide is formed exclusively: 11 grams were obtained, melting at 63°, and also confirmed by a complete analysis. The imidechloride has therefore been decomposed according to the following equation:



$$\begin{array}{l} CH_3\text{-}C_6H_4\text{-}N{=}C^{\diagup Cl} \\ \qquad\qquad\quad | \\ \qquad\quad CH_3\text{-}CO \end{array} + 2H_2O = CH_3\text{-}C_6H_4N{=}C\begin{matrix}OH\\H\end{matrix} + HCl + CH_3COOH.$$

This decomposition is not surprising when one considers that pyruvic-anilidimidechloride is decomposed by alcohol in a similar manner (p. 127); and although on treating this imidechloride with water pyruvic anilide is the chief product (p. 129), formanilide is also formed, but in slight amount only.

The above crude pyruvic-*o*-toluideimidechloride can however be converted in part into pyruvic-*o*-toluide by pouring it into a large amount of water. The yield is small (about 15%), and form-*o*-toluide is present in larger quantiy, and it was not found possible to effect a separation of these two products in a simple manner. A polymeric pyruvic-*o*-toluide could however be isolated as follows. The crude imidechloride was poured into a large amount of water, and allowed to stand for an hour. The mixture, consisting also of some isonitrile, was extracted with ether, and the ethereal solution treated with dilute sodic hydrate. The alkaline solution was thereupon again extracted with fresh ether. On acidifying nothing separates out, but ether extracts a substance, which is very soluble in water (melting point 62°, crystallizing in six-sided plates).

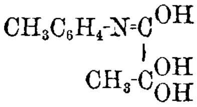
On drying the ethereal solution with calcic chloride, a flaky substance all at once begins to separate out in large amount. Recrystallized twice from alcohol, it was obtained in colorless needles, melting at 177°.

0.2032 gram substance, dried at 110°, gave 0.5079 gram CO_2 and 0.1153 gram H_2O.

0.2244 gram substance, dried at 110°, gave 15.5 c.c. moist nitrogen at 16° and 752 mm.

	Theory for $C_{10}H_{11}NO_2$.	Found.
C	67.79	68.16
H	6.21	6.34
N	7.91	7.97

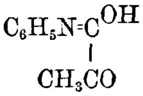
The substance is insoluble in water and ether, easily soluble in hot alcohol. It dissolves in dilute sodic hydrate, and comes down unchanged on acidifying. It is probable that the above mentioned substance, melting at 62°, is a hydrate,



$$\begin{array}{l} CH_3C_6H_4\text{-}N\text{=}C^{OH} \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad CH_3\text{-}C\begin{smallmatrix}OH\\OH\end{smallmatrix} \end{array}$$

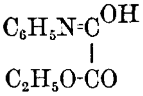
which loses water under the influence of the dehydrating agent, calcic chloride, and at the same moment polymerization takes place.

It has already been shown in an entirely analogous manner that, on treating pyruvicanilide,



$$\begin{array}{c} C_6H_5N\text{=}C^{OH} \\ | \\ CH_3CO \end{array}$$

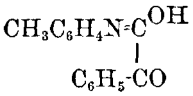
and oxanilethane,



$$\begin{array}{c} C_6H_5N\text{=}C^{OH} \\ | \\ C_2H_5O\text{-}CO \end{array}$$

with alkalies, polymerization takes place (pp. 125 and 130).

Benzoylformic-o-toluide,

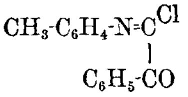


$$\begin{array}{c} CH_3C_6H_4N\text{=}C^{OH} \\ | \\ C_6H_5\text{-}CO \end{array}$$

As was to be expected, benzoylchloride adds itself much more slowly than acetylchloride to the isonitriles. On this account, experiments undertaken with the object of adding benzoylchloride to phenylisocyanide have not been successful. The addition takes place very slowly at 100°, and at the same time so much polymerization (resin formation) results that the presence of benzoylformicanilide (not as yet known) could not be proved.

The case is quite different if *o*-tolylisocyanide be taken, instead of the lower homologue, as this substance does not polymerize so readily. Five grams *o*-tolylisocyanide and one molecule of benzoylchloride were heated for a day on a water bath, and thereupon 6–8 volumes of hot ligroine (bpt. 70°–80°) added. This causes the separation of polymerization products as resins, which are got rid of by filtering hot.

After distilling off the ligroine, water is added in order to decompose the imidechloride,



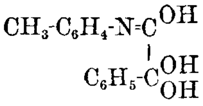
$$\begin{array}{r} CH_3\text{-}C_6H_4\text{-}N{=}C^{Cl} \\ | \\ C_6H_5\text{-}CO \end{array}$$

formed. The mixture is then heated on a water bath until no more smell of benzoylchloride is noticed. After extracting with ether, and washing the ether solution with soda, it is dried with calcic chloride. On concentrating and cooling, the ethereal solution benzoylformic-*o*-toluide separates out in large quantity (3.5 grams). Recrystallized twice from ether and ligroine, it was obtained in colorless needles (3 grams), melting at 108°. The substance burns with great difficulty on analysis, for which it was dried at 80°–90.°

0.1566 gram substance gave 0.4313 gram CO_2 and 0.0792 gram H_2O.
0.2557 gram substance gave 13 c.c. moist nitrogen at 14° and 754 mm.

	Theory for $C_{15}H_{13}NO_2$.	Found.
C	75.31	75.11
H	5.44	5.61
N	5.85	5.93

Benzoylformic-*o*-toluide dissolves on gentle warming in sodic hydrate, forming thus in all probability a salt of the hydrate,

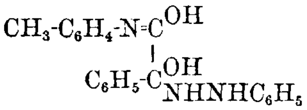


$$\begin{array}{r} CH_3\text{-}C_6H_4\text{-}N{=}C^{OH} \\ | \\ C_6H_5\text{-}C^{OH}_{OH} \end{array}$$

On acidifying it comes down unchanged. It is insoluble in water, but easily soluble in hot ether and alcohol, and crystallizes out in needles.

The substance is very stable in the presence of concentrated sulphuric or hydrochloric acid, even at 100°. Boiling with an excess of sodic hydrate splits off *o*-toluidine, but no benzoylformic acid is obtained in this way.

Benzoylformic-o-toluide Phenylhydrazonehydrate,



$$\begin{array}{l} CH_3\text{-}C_6H_4\text{-}N{=}C^{OH} \\ \qquad\qquad\quad | \\ \qquad\quad C_6H_5\text{-}C^{OH}_{NHNHC_6H_5} \end{array}$$

One molecule of phenylhydrazine is added to a lukewarm (30°) very concentrated solution of benzoylformic-*o*-toluide, and the mixture cooled to 0°.

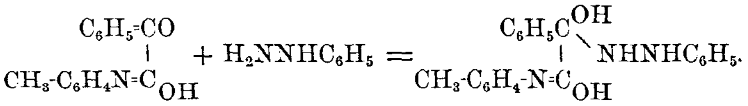
A white crystalline granular precipitate — the hydrazonehydrate — separates out, which was well washed, dried on a porous clay plate and finally for two hours over H_2SO_4 in a vacuum.

0.1563 gram substance gave 0.4134 gram CO_2 and 0.0879 gram H_2O.

0.1976 gram substance gave 20.6 c.c. moist nitrogen at 19° and 749 mm.

	Theory for $C_{21}H_{21}N_3O_2$.	Found.
C	72.62	72.13
H	6.05	6.25
N	12.10	11.90

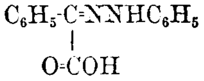
Phenylhydrazine has thus simply added itself to the carbonyl group present in benzoylformic-*o*-toluide,



$$\begin{array}{l} C_6H_5\text{-}CO \\ \qquad\quad | \\ CH_3\text{-}C_6H_4N{=}C_{OH} \end{array} + H_2NNHC_6H_5 = \begin{array}{l} C_6H_5C^{OH}\diagdown \\ \qquad\quad |\quad NHNHC_6H_5. \\ CH_3\text{-}C_6H_4\text{-}N{=}C_{OH} \end{array}$$

That no salt-like compound is formed in this case is shown by the fact that sodic hydrate does not split it into the components.

The hydrazonehydrate loses water on standing, or very quickly at 60°, and becomes yellow and sticky; also on heating much above 30° in solution it is converted into a yellow hydrazone, which was not further investigated. 1.3 grams hydrazonehydrate were heated gently in alcoholic solution with sodium ethylate (from 0.5 gram sodium), and then the alcohol distilled off. After adding water and extracting with ether, the alkaline solution was acidified with hydrochloric acid, and a yellow bulky precipitate obtained. It was filtered off, dissolved in soda, reprecipitated, and finally crystallized from acetic acid. Yellow needles were obtained melting at 153°, and identical in every respect with a product, benzoylformic acid phenylhydrazone,



$$\begin{array}{l} C_6H_5\text{-}C{=}N\text{-}NHC_6H_5 \\ \quad\;\; | \\ \quad O{=}COH \end{array}$$

which Elbers * first obtained from phenylglyoxylic acid and phenylhydrazine. Hence it is proved that the above two substances are in reality derivatives of benzoylformic acid.

III. On *p*-Tolylisocyanide, $CH_3\text{-}C_6H_4\text{-}N{=}C{=}$.

Preparation of p-Tolylisocyanide.—This substance was obtained from *p*-toluidine, etc., exactly as above in the case of the ortho derivative, except that the isonitrile was not distilled over with steam, which probably would have been an advantage. 22 grams crude *p*-tolylisocyanide were obtained from 100 grams of *p*-toluidine; it was distilled twice under reduced pressure. In the first distillation, a large amount of residue remained; on the second distillation, the isonitrile came over at 99° at 36 mm., and no residue was left. It is a colorless oil, which on standing becomes colored greenish yellow.

0.1137 gram substance gave 0.3398 gram CO_2 and 0.0639 gram H_2O.

0.2117 gram substance gave 22 c.c. moist nitrogen at 20° and 752 mm.

	Theory for C_8H_7N.	Found.
C	82.05	81.50
H	5.98	6.24
N	11.97	11.77

p-tolylisocyanide has a smell which is markedly different from that of the other two isonitriles obtained above; yet it is difficult to describe in words the difference. The smell is at first pleasant and aromatic, but also gradually excites nausea.

Isocyan-p-tolylchloride, or p-Tolylimidocarbonylchloride,
$CH_3\text{-}C_6H_4N{=}C{=}Cl_2$.

The preparation of this substance is entirely analogous to that of the corresponding ortho derivative. A colorless sharp-smelling oil is obtained, which attacks the eyes, and boils at 225°–226° (uncorr.).

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* Ann. Chem. (Liebig), CCXXVII. 341.

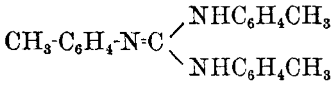
0.2486 gram substance gave 0.4661 gram CO_2 and 0.0861 gram H_2O.

0.1855 gram substance gave 0.2865 gram AgCl on ignition with CaO.

0.2704 gram substance gave 19 c.c. moist nitrogen at 22° and 750 mm.

	Theory for $C_8H_7NCl_2$.	Found.
C	51.06	51.13
H	3.73	3.84
N	7.45	7.85
Cl	37.76	38.20

Isocyan-*p*-tolylchloride when treated with *p*-toluidine is converted into *p*-tritolylguanidine hydrochloride. In order to obtain the free base,



$$CH_3\text{-}C_6H_4\text{-}N{=}C\begin{matrix}\diagup NHC_6H_4CH_3\\ \diagdown NHC_6H_4CH_3\end{matrix}$$

the solution is made slightly alkaline, and the excess of *p*-toluidine driven over with steam.

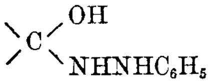
The residue was recrystallized from alcohol, and colorless needles obtained, melting at 123°, and identical in every respect with a *p*-tritolylguanidine obtained by Merz and Weith.*

CONCLUDING REMARKS.

A. *On Geometrical Isomerism of the Hydroxylamine Derivatives.*

The following new observations have been made in the above experimental portion, which find application in many directions.

1. That a carbonyl group, $\rangle C{=}O$, can by the addition of water attain strong acid properties (p. 123). 2. That a carbonyl group always reacts with phenylhydrazine, forming in the first place an addition product,



$$\begin{matrix}\diagdown\\ \diagup\end{matrix}C\begin{matrix}\diagup OH\\ \diagdown NHNHC_6H_5\end{matrix}$$

(pp. 121, 131, 148). 3. A spontaneous or easy splitting off of HX, H_2S, H_2O, from one and the same carbon atom (p. 137). 4. The conversion of imidechlorides,

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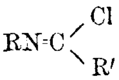
* Zeitschrift für Chemie, 1868, p. 610.



$$RN{=}C\begin{matrix} Cl \\ R' \end{matrix}$$

by the elimination of alkylchloride, R′Cl, into isonitriles, $RN{=}C{=}$ (pp. 127, 128).

In this case two carbon atoms bound singly to each other are torn apart, which shows how strong a tendency must exist for a decomposition in this direction. A similar reaction has already been observed by myself in the case of dibenzoyl, diacetyl, and dicarboxyl-acetacetic ether.[*]

That chloralhydrate and glyoxylic and mesoxalic acid contain two hydroxyl groups bound to the same carbon atom is pretty generally regarded as proved. Very recently Zincke and Arust[†] have shown that tetrachlor-*o*-diketohydronaphthaline forms hydrates and alcoholates, where the water and alcohol respectively cannot be present as crystal water.

There exist already a number of examples in chemical literature where a substance containing carbonyl groups attains thereby acid properties. Thus, for example, triquinoyl,[‡] $C_6O_6 + 8\ H_2O$, and leuconic acid, $C_5O_5 + 4\ H_2O$, of which the last named has been especially studied by Nietzki and Benckiser.[§] These substances, being strong acids, cannot contain all the water as crystal water, but they are to be regarded as hydroxylated compounds; $C_6O_6 + 8\ H_2O$, e. g., is very probably dodekoxyhexamethylene, $C_6(OH)_{12} + 2\ H_2O$.

In a like manner diacetyl, $CH_3{-}CO{-}CO{-}CH_3$, which was discovered almost simultaneously by v. Pechmann[‖] and by Fittig,[¶] possesses marked acid properties. It can be separated completely from alcohol by concentrating a sodic carbonate solution of it on a water bath.[**] Diacetyl itself forms hydrates and alcoholates, decomposed by sulphuric acid, which have as yet not been further studied.[**] It follows, therefore, that this substance by taking up water becomes an acid stronger than carbonic acid: it cannot be decided yet whether the acid resulting has the formula

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[*] Ann. Chem. (Liebig), CCLXVI. 101, 105, 107.

[†] Ibid., CCLXVII. 329.

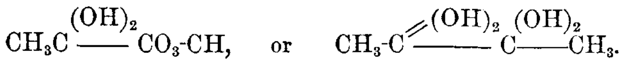
[‡] Nietzki and Benckiser, Ber. d. Chem. Ges., XVIII. 504, 1842.

[§] Ber. d. Chem. Ges., XIX. 301.

[‖] Ibid., XX. 3163, 3213.

[¶] Ibid., XX. 3184.

[**] Ibid., XXI. 1411, 1412, v. Pechmann.

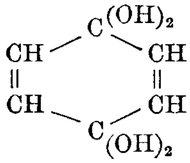


$$CH_3C\overset{(OH)_2}{\text{——}}CO_3\text{-}CH, \quad \text{or} \quad CH_3\text{-}C\overset{\nearrow(OH)_2}{=\!=\!=}\overset{(OH)_2}{C}\text{——}CH_3.$$

The above observations also suffice to clear up the hitherto enigmatic behavior of quinone toward hydrogen haloids and water. Hesse * and Ciamician † have shown that water converts quinone into hydroquinone, while Levy and Schultz, ‡ as well as Sarauw, § have converted quinone by means of hydrobromic and hydrochloric acid into chlor- and bromhydroquinone respectively.

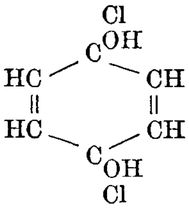
I supposed formerly ‖ that these reactions were to be explained by an addition of water and halogen hydride respectively to the two pairs of double bonds present in quinone.

That this, however, is not the case, will be soon shown in detail by Mr. Clark. It seems to me, therefore, very probable that the peculiar behavior of quinone towards water and hydrogen haloids is due to the presence of the two carbonyl groups in this compound. Two molecules of water or of hydrochloric acid add themselves to quinone, forming



I.

and



II.

which then lose H_2O_2 and Cl_2 respectively, forming hydroquinone: the chlorine set free then reacts further, giving chlorhydroquinone and hydrochloric acid. That the intermediate products I. and II. should lose H_2O_2 or Cl_2 so readily, and go over into benzene derivatives, is not surprising when one considers how easily Δ 2,5 dihydroterephthalic acid goes over into terephthalic acid.¶

The fact that a carbonyl group reacts with phenylhydrazine, forming an addition product, as well as the behavior of this group towards water and alkalies, suffices to throw an entirely new light

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* Ann. Chem. (Liebig), CCXX. 367.

† Gazzetta Chim., XVI. 111.

‡ Ann. Chem. (Liebig), CCX. 133.

§ Ibid., CCIX. 93.

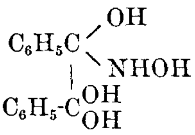
‖ Amer. Chem. Journal, XIII. 427.

¶ v. Baeyer, Ann. Chem. (Liebig), CCLI. 293.

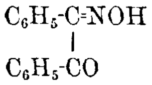
on the reaction which takes place between benzil and hydroxylamine. As is well known, Auwers and v. Meyer have obtained two isomeric benzilmonoximes, and three isomeric benzildioximes. They sought, in the first place,[*] to explain this isomerism by a different grouping of the atoms in space, but soon gave up this explanation as insufficient,[†] especially because of the observations of Hantzsch. The latter, together with Werner,[‡] has brought forward a new hypothesis to explain this isomerism, which depends upon the assumption that space isomers of trivalent nitrogen can exist.

The experimental proof, however, upon which everything depends, that the three dioximes, for example, have the same chemical constitution, cannot be regarded as absolutely settled.

From the observations developed in this paper, hydroxylamine (one molecule) will react with benzil, forming in the first place an addition product,

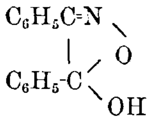


which can then lose water (two molecules) in two different ways, giving



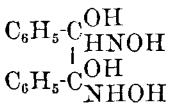
$$\begin{array}{l} C_6H_5\text{-}C{=}NOH \\ \quad\ | \\ C_6H_5\text{-}CO \end{array}$$

and



γ oxime, I. α oxime, II.

In a like manner two molecules of hydroxylamine will react on benzil, forming first the addition product,



$$\begin{array}{l} C_6H_5\text{-}C\begin{smallmatrix}OH\\ HNOH\end{smallmatrix} \\ \qquad | \\ C_6H_5\text{-}C\begin{smallmatrix}OH\\ NHOH\end{smallmatrix} \end{array}$$

which can then lose two molecules of water in three different ways:

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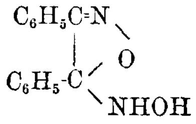
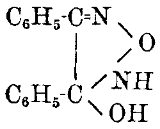
[*] Ber. d. Chem. Ges., XXI. 946, 3510, XXII. 705.

[†] Ibid., XXIII. 2405.

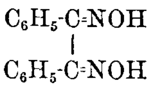
[‡] Ibid., XXIII. 11.



α dioxime III.



γ dioxime IV.



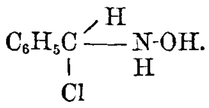
$$\begin{array}{l} C_6H_5\text{-}C{=}NOH \\ \quad | \\ C_6H_5\text{-}C{=}NOH \end{array}$$

β dioxime V.

The oximes I., II. and III.–V., respectively, can naturally be converted into one another without molecular rearrangement by the addition of water or halogen hydride, and the splitting off again in a different way. The entire experimental work of Auwers, V. Meyer, and others, on the oximes of benzil was very carefully studied, and not a single fact found therein which could not be explained by the above formulæ, which are chemically different. This shows on what an uncertain basis the assumed geometrical isomerism of these substances rests.*

A similar relationship exists in the case of the oximes of benzaldehyde: the α oxime is converted by means of hydrochloric acid, as Beckmann † has shown, into a solid β isomer.

It is highly probable, in the first place, that the product obtained with hydrochloric acid is not a salt, but an addition product,



On pouring this into sodic carbonate, it loses HCl in a different way forming the oxid,‡ $C_6H_5\text{-}\underset{\diagup\diagdown}{C}\text{-}NHOH$, or β oxime. That a splitting off of HCl can take place in this manner, and often spontaneously, has been shown above (pp. 136, 150).

The ready conversion of β benzaldoxime into benzonitrile is self-evident in the case of the above oxid formula. Furthermore, the simultaneous formation of nitrogen and oxygen ethers on treating the β oxime with alkyliodides § is also explained.

That the two oximes of benzaldehyde both contain a hydroxyl group was first shown by Goldschmidt,* and later proved with all precision by Hantzsch.† Up to the present time no fact exists which could be brought against the above formula for the β oxime, and the great majority are explained more simply by it than by the assumption of geometrical isomerism of the nitrogen. This suffices to show on how uncertain a basis the assumption rests that the two oximes of benzaldehyde are alike constituted.

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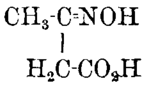
* Cf. Claus, J. pr. Chemie, [2.], XLV. 1–20.

† Ber. d. Chem. Ges., XXII. 430.

‡ I propose the name oxid for the group -NHOH, leaving the name oxime for the group =NOH: this is entirely analogous to the names hydrazide and hydrazone for the groups $C_6H_5NH\text{-}NH\text{-}$ and $C_6H_5NH\text{-}N{=}$, respectively.

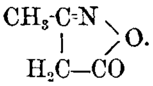
§ Goldschmidt, Ber. d. Chem. Ges., XXIII. 2176.

Finally, the presence of geometrical isomerism has been assumed in a number of cases where it certainly does not exist: so, for example, in the case of the so called β oximidobutyric acid,



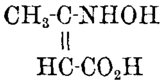
$$\begin{array}{c} CH_3\text{-}C{=}NOH \\ | \\ H_2C\text{-}CO_2H \end{array}$$

and its anhydride,‡



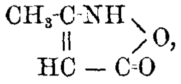
$$\begin{array}{l} CH_3\text{-}C{=}N\diagdown \\ \quad\;\; | \qquad\; \rangle O. \\ \;\; H_2C{-}CO\diagup \end{array}$$

These substances cannot possess the constitution given them: it follows with certainty, from the work on acetoacetic ether,§ that the substances have the following constitution,



$$\begin{array}{c} CH_3\text{-}C\text{-}NHOH \\ \| \\ HC\text{-}CO_2H \end{array}$$

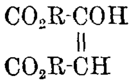
and



$$\begin{array}{l} CH_3\text{-}C\text{-}NH\diagdown \\ \qquad \| \qquad\;\; \rangle O, \\ \quad HC - C{=}O\diagup \end{array}$$

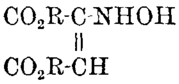
where a geometrical isomerism on account of the nitrogen is impossible.

Also the two substances that have been described as oximidosuccinic acids,‖ are certainly of different chemical constitution. Oxalacetic ether,



$$\begin{array}{c} CO_2R\text{-}COH \\ \| \\ CO_2R\text{-}CH \end{array}$$

must react with hydroxylamine, just as acetacetic ether with phenylhydrazine, and form an oxid of the constitution,



$$\begin{array}{c} CO_2R\text{-}C\text{-}NHOH \\ \| \\ CO_2R\text{-}CH \end{array}$$

i. e. a fumaric acid derivative.

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* Ber. d. Chem. Ges., XXIII. 2176.

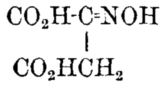
† Hantzsch, Ber. d. Chem. Ges., XXIV. 16.

‡ Ibid., XXIV. 497.

§ Ann. Chem. (Liebig), CCLXVI. 64 and 70.

‖ Cramer, Ber. d. Chem. Ges., XXIV. 1198.

On the other hand, the product obtained from succinosuccinic ether is alone to be regarded as oximidosuccinic acid,



$$\begin{array}{c} CO_2H\text{-}C{=}NOH \\ | \\ CO_2HCH_2 \end{array}$$

That, however, the one product can, by addition of water or of HCl, and the splitting off again of these reagents, be converted into the other, is readily seen.

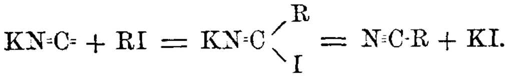
With regard to the so called geometrical isomeric dioximidosuccinic acids,* it can be said that the isomers discovered have not been proved to have the same constitution. The above observations in the case of the oximes of benzil, as well as the possibility of lactone formation, complicate matters here to such an extent that much more experimental material must be at hand in order to decide the question.

B. *On the Nature of Prussic Acid.*

From the above experiments, and the work on acetacetic ether, it has become very probable that prussic acid has the formula $HN{=}C{=}$, and, consequently, that the metal in its salts is bound to nitrogen, $M\text{-}N{=}C{=}$.

The physical properties of prussic acid, boiling point 26.°2, specific gravity 0.697, and the poisonous properties, all tend to show that this substance is the first member of the isonitrile, $R\text{-}N{=}C{=}$, series. At present experiments are being undertaken with the object of obtaining the actual formonitrile, $H\text{-}C{\equiv}N$, by the reduction of cyanogen chloride or iodide. It is to be expected that this substance will be neutral, and that it will possess a much higher boiling point and specific gravity than prussic acid.

Potassium cyanide,† $K\text{-}N{=}C{=}$, reacts with alkyliodides, owing to the energy of the bivalent carbon atom present, chiefly as follows:



$$KN{=}C{=} + RI = KN{=}C\begin{array}{l} \diagup R \\ \diagdown I \end{array} = N{\equiv}C\text{-}R + KI.$$

Addition Product. Alkylcyanide.

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* Söderbaum, Ber. d. Chem. Ges., XXIV. 1215.

† It would be more logical to call this substance potassic isocyanide, since it does not belong to the cyanogen ($\text{-}C{\equiv}N$), but to the isocyanogen ($\text{-}N{=}C{=}$) compounds. It is however questionable whether such a change would be feasible at present.

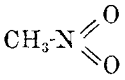
Simultaneously with this reaction, but in subordinate amount, a *direct* replacement of the potassium *always* takes place; so that an alkylcyanide results as the chief product, but an alkylisocyanide is always noticed as a side product, as has been observed by Dumas, Malaguti, Hofmann, Gautier, and others.

That the silver salt, $AgN{=}C{=}$, should show a different behavior towards alkyliodides, is also very clear;[*] first, because silver is less positive than potassium, and consequently the bivalent carbon atom present in both salts must be less reactive in the case of silver cyanide; secondly, a direct replacement of the metal will take place more readily in the case of the silver salt.

That, however, it may happen, even with the silver salt, that no direct replacement of the metal takes place, is shown by the behavior of cyanide of silver towards acetyl- and benzoyl-chlorides. In these instances, the isonitriles, $CH_3CO\text{-}N{=}C{=}$ and $C_6H_5CO\text{-}N{=}C{=}$, are not formed, as Gautier[†] thought probable in 1869, but $CH_3\text{-}CO\text{-}C{\equiv}N$ and $C_6H_5CO\text{-}C{\equiv}N$ are the products[‡] obtained.

There exists at the present time in organic chemistry an hypothesis that a hydrogen atom bound directly to carbon can attain acid properties when one or more negative groups are also bound to the same carbon atom. It is said that the negative group exerts an "acid-making" influence on the hydrogen atom, which extends, however, only to hydrogen bound to the same carbon atom as the negative radical.

This hypothesis has absolutely no justification, and is entirely illogical. It has already been shown that a methylene group between two carbonyl groups, $CO\text{-}CH_2\text{-}CO$, has no acid properties whatever.[§] Furthermore, it is to be observed that in other cases, where it has been assumed that a hydrogen atom bound directly to carbon attains acid properties, the negative group present contains either oxygen or nitrogen, e. g. in nitro methane,



$$CH_3\text{-}N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$$

and in $H\text{-}C{\equiv}N$. Now the groups Cl, Br, and F are undoubtedly more negative than the cyanogen group, $\text{-}C{\equiv}N$, and possibly more so than the nitro group, $\text{-}NO_2$; notwithstanding this, chloroform, $CHCl_3$, bromoform, $CHBr_3$, and fluoroform, CHF_3, although we have in these instances three strong electro-negative groups bound to a carbon atom containing hydrogen, are all perfectly neutral substances; whereas it has been assumed that in $H\text{-}C{\equiv}N$ the presence of the group ${\equiv}N$, which can be regarded as only very slightly negative, renders the hydrogen bound to carbon acid in its nature!

---

[*] Cf. Ann. Chem. (Liebig), CCLXVI. 137.

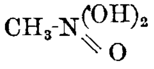
[†] *Loc. cit.*, XVII. 208.

[‡] Claisen, Ber. d. chem. Ges., X. 845, XI. 620, 1563.

[§] Ann. Chem. (Liebig), CCLXVI. 67 and 113.

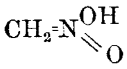
It is highly improbable that sodic nitromethane possesses the constitution $CH_2Na\text{-}NO_2$:[*] the formation of bromnitromethane, $CH_2Br\text{-}NO_2$, from it by means of bromine proves nothing with regard to the constitution of the sodium salt.[†]

Assuming that nitromethane possesses the constitution $CH_3\text{-}NO_2$, it is very well possible that on treating it with alkalies water adds itself (as in the case of a CO group) to the nitro group,



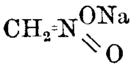
$$CH_3\text{-}N\begin{matrix}(OH)_2\\ \diagdown O\end{matrix}$$

and that this is split off again in another manner,



$$CH_2{=}N\begin{matrix}OH\\ \diagdown O\end{matrix}$$

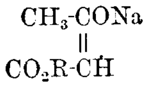
so that the sodium salt has the constitution



$$CH_2{=}N\begin{matrix}ONa\\ \diagdown O\end{matrix}$$

C. *On Acetacetic Ether.* (*Supplementary.*)

In the first place, it may be remarked that the addition of acid haloids to isonitriles described above is to be regarded as a very essential confirmation of my work on acetacetic ether, in which I proved experimentally that in the action of alkyliodides, as well as of acid haloids, on sodium acetacetic ether, not a direct replacement of the metal, but an addition, takes place. The experiments show that the double bond present in sodium acetacetic ether,



$$\begin{matrix}CH_3\text{-}CONa\\ \| \\ CO_2R\text{-}CH\end{matrix}$$

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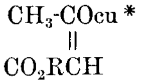
[*] V. Meyer, Ann. Chem. (Liebig), CLXXI. 33.

[†] Amer. Chem. Journ., XIII. 427.

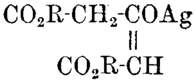
is more reactive than the bivalent carbon atom present in the isonitriles, $R\text{-}N{=}C{=}$, which must be due to the more positive condition of the molecule; if, however, the copper salt,



$$\begin{array}{c} CH_3\text{-}COcu\ ^{*} \\ \| \\ CO_2RCH \end{array}$$

be taken, we have a substance whose reactivity is about the same as that of the isonitriles.

The objection of v. Pechmann,[†] that silver acetonedicarboxylic ether,

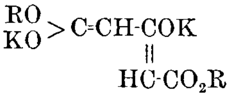


$$\begin{array}{c} CO_2R\text{-}CH_2\text{-}COAg \\ \| \\ CO_2R\text{-}CH \end{array}$$

reacts with alkyliodides, forming the same product as the sodium salt, is without weight, since it has already been proved[‡] that copper, lead, and mercuric acetacetic ether react with alkyliodides and acid haloids, forming addition products, i. e. the metal is not directly replaced. It is therefore to be expected that a silver salt will show a similar behavior.

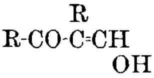
That in the case of silver salts the metal is not always directly replaced is evident from the behavior of silver cyanide, $AgN{=}C{=}$, towards benzoyl- and acetylchloride (*vide* p. 157, and cf. J. pr. Chem. [2.], 42, 177).

Furthermore, the fact that acetonedicarboxylic ether forms a dipotassium salt[§] cannot be considered as evidence against its hydroxylated nature, since this salt can very well possess the constitution,



$$\begin{array}{l} \begin{matrix} RO \\ KO \end{matrix} > C{=}CH\text{-}COK \\ \qquad\qquad\quad \| \\ \qquad\qquad HC\text{-}CO_2R \end{array}$$

V. Pechmann[‖] has just proved, exactly as Claisen[¶] had already done in the case of ketoaldehydes,



$$\begin{array}{l} \qquad\quad R \\ R\text{-}CO\text{-}C{=}CH \\ \qquad\qquad\quad OH \end{array}$$

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[*] Means half an atom of copper Cu''.

[†] Ber. d. chem. Ges., XXIV. 4097.

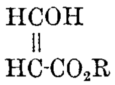
[‡] Ann. Chem. (Liebig), CCLXVI. 59 and 121.

[§] Ber. d. chem. Ges., XXIV. 4096.

[‖] Ibid., XXV. 1040.

[¶] Sitzungsber. der bayer. Akad. d. Wiss., XX. 463.

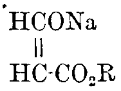
that formyl-acetic ether contains a hydroxyl group,



$$\begin{array}{l} HCOH \\ \;\| \\ HC\text{-}CO_2R \end{array}$$

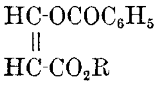
It seems to me, therefore, now only a question of time until it will be generally accepted that the so called 1,3 and 1,4 diketones, as acetylacetone, $CH_3COH{=}CH\text{-}CO\text{-}CH_3$, and acetonylacetone, $CH_3COH{=}CH\text{-}CH{=}COH\text{-}CH_3$, as well as acetacetic ether, are hydroxylated compounds.

Although v. Pechmann has shown that sodic formylacetic ether,



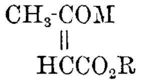
$$\begin{array}{l} HCONa \\ \;\| \\ HC\text{-}CO_2R \end{array}$$

when treated with benzoylchloride, is converted into



$$\begin{array}{l} HC\text{-}OCOC_6H_5 \\ \;\| \\ HC\text{-}CO_2R \end{array}$$

i. e. that a *direct* replacement of the metal by benzoyl has taken place, I have shown, on the other hand, in just as decisive a manner, that, on treating acetoacetic ether salts,*



$$\begin{array}{l} CH_3\text{-}COM \\ \qquad\| \\ \quad HCCO_2R \end{array}$$

with acid chlorides, *no direct* substitution of the metal takes place.

Furthermore, I have also shown some time ago that sodic succinosuccinic ether and sodic dihydrodioxypyromellithic ether,† which substances are more closely related to acetoacetic ether than formylacetic ether, behave towards alkyliodides and acid chlorides in a different manner from sodic acetoacetic ether. This can only be due to the fact that the double bond present in sodic acetacetic ether is more reactive than in the other cases.

V. Pechmann's experiments,‡ where he treats sodic acetacetic ether in aqueous solution with benzoylchloride, and with chlorocarbonic ether, are to be regarded as a repetition of my experiments, since the process of the reaction must be the same whether the operation be carried on in absolute ethereal or in aqueous solution. The behavior of sodic acetacetic ether towards acetic anhydride * can also be easily explained by a twofold addition.

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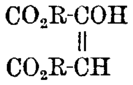
* Ann. Chem. (Liebig), CCLXVI. 121.

† Ibid., CCLVIII. 261.

‡ Ber. d. chem. Ges., XXV. 410, 1045.

Finally, the action of phenylhydrazine on acetacetic ether cannot be regarded as taking place in a manner analogous to the three cases discovered above (p. 150), i. e. that the first named substance simply adds itself to the carbonyl group. Oxalacetic ether,



$$\begin{array}{c} CO_2R\text{-}COH \\ \| \\ CO_2R\text{-}CH \end{array}$$

forms, as W. Wislecenus † has shown, with phenylhydrazine a salt-like compound, which is instantly split into its components by alkalies, whereas the three hydrazonehydrates described in this paper are not changed by alkalies.

A number of the objections brought forward by Brühl ‡ seem to show that he has not fully understood my work on acetacetic ether; as, for instance, his remarks on the proof "that a methylene group between two carbonyl groups possesses no acid reaction."

I have shown, 1st, that malonic ether is neutral, i. e. it possesses no acid properties; 2d, that sodic malonic ether is instantly decomposed by water, like sodiumethylate; 3d, that the free malonic ether shows a behavior entirely different from acetacetic ether; and consequently, 4th, proved that malonic ether forms a salt *only in case sodic ethylate* is present.

That many acids exist which do not react with sodium in absolute ethereal solution, seems to weaken the above proof in Brühl's ‡ opinion; but this fact has absolutely no bearing on the point under discussion. If, on the other hand, it is proposed to discuss the question whether a substance can be an acid, which is not soluble in soda or caustic soda, or which is not thereby converted into an insoluble salt, that is another matter.

Although Brühl finds the refractive index of acetacetic ether to be in favor of the ketone formula of this substance, I am able to bring forward another physical property of this substance which points to the contrary, namely, that acetacetic ether is an electrolyte, and therefore an acid; whereas malonic ether is a non-electrolyte, and consequently not an acid.

This shows how uncertain the conclusions are which can be drawn from the physical properties of a substance with regard to its chemical constitution, — as has already been shown by the discussion on the constitution of benzene.

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* *Loc. cit.*, XXV. 1046.

† Ber. d. chem. Ges., XXIV. 3006.

‡ Ibid., XXV. 366.

Finally, the following supplementary remarks are made with reference to the paper on acetacetic ether.[*] The substance described as phenylhydrazine β-ethylic carboxylate (p. 107) is identical in every respect with Heller's phenylcarbazinic ether;[†] recrystallized from water, the melting point 85° was obtained, and the substance, owing to a slight oxidation, becomes colored.

The melting point of (1) methyl pyrrol (2) carboxylic (4) acetic ether (page 86), is incorrectly given 186°; it should be 168°.

It should also be stated that Franchimont and Klobbie[‡] have succeeded, by employing a different method from mine (p. 113, cf. also p. 106), in converting malonic ether into a nitro derivative. I regret that this paper should have been overlooked.

The interesting paper of Conrad and Brückner,[§] "Ueber die Geschwindigkeit der Verlaufes der Acetessigäther Synthesen," which appeared after I had sent off my paper to the Annalen, is entirely in accord with the results obtained in my work.

In the above work on bivalent carbon, which will be continued, I have been most zealously assisted by Dr. M. Ikuta, to whom I wish here to express my warmest thanks.

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[*] Ann. Chem. (Liebig), CCLXVI. 52–138.

[†] Ann. Chem. (Liebig), CCLXIII. 278.

[‡] Recueil de trav. chim. de Pays Bas, VIII. 283 (1889); cf. Franchimont, Revue Scientif., 1890.

[§] Zeitsch. für physikal. Chemie, VII. 283.

XI.

NOTE ON THE REPRESENTATION OF ORTHOGONAL MATRICES.

By Henry Taber, Clark University.

Presented May 24, 1892.

If ϕ is an orthogonal matrix of which -1 is not a latent root, we may put

$$\Upsilon = \frac{1-\phi}{1+\phi};$$

whence follows

$$\text{tr.}\,\Upsilon = \frac{1-\text{tr.}\,\phi}{1+\text{tr.}\,\phi} = \frac{1-\phi^{-1}}{1+\phi^{-1}} = \frac{\phi-1}{\phi+1} = -\Upsilon;$$

and we have

$$\phi = \frac{1-\Upsilon}{1+\Upsilon}.$$

This is Cayley's well known representation of an orthogonal matrix in terms of a skew symmetric matrix. If -1 is a latent root of ϕ, but not 1, $-\phi$ will be an orthogonal matrix of which 1 is a latent root, but not -1; therefore, $-\phi$ may be represented as above, giving

$$\phi = -\frac{1-\Upsilon}{1+\Upsilon}.$$

Thus the expression

$$\pm\frac{1-\Upsilon}{1+\Upsilon}$$

will, for a proper value of the skew symmetric matrix Υ, give all orthogonal matrices except those which have as latent roots both ± 1. Such of these matrices as are real, and of which the multiplicity of the latent root -1 is even, and, more generally, any real proper orthogonal matrix, can, I find, be represented as an exponential function of a real skew symmetric matrix.

Thus, if ϕ is any real proper orthogonal matrix, a real skew symmetric matrix θ can always be found such that

$$\phi = e^{\theta},$$

where e denotes the base of the Napierian logarithms ; e^{θ} is of course defined as the exponential series, which is convergent, and for which an expression may be obtained by Sylvester's theorem. This function of θ, for all real skew symmetric matrices, gives only real proper orthogonal matrices. Therefore by taking successively all possible real skew symmetric matrices, all possible real proper orthogonal matrices may thus be found.

POSTSCRIPT.

Real improper orthogonal matrices are of two kinds: of the first kind are those real improper orthogonal matrices of which unity is not a latent root, or of which the multiplicity of the latent root unity is even ; real improper orthogonal matrices of the second kind are those of which the multiplicity of the latent root unity is odd.

If ϕ is a real improper orthogonal matrix of the first kind, a real skew symmetric matrix θ can always be found such that

$$\phi = -e^{\theta}.$$

This function of θ, for all real skew symmetric matrices, gives only real improper orthogonal matrices of the first kind.

A real improper orthogonal matrix of the second kind cannot be represented as a function of any real skew symmetric matrix.

WORCESTER, MASS., July 12, 1892.

XII.

CONTRIBUTION FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

DESCRIPTIONS OF NEW PLANTS COLLECTED IN MEXICO BY C. G. PRINGLE IN 1890 AND 1891, WITH NOTES UPON A FEW OTHER SPECIES.

BY B. L. ROBINSON.

Presented by George Lincoln Goodale, June 15, 1892.

CLEOME POTOSINA. Herbaceous, two feet high: stem purplish, striate, moderately branched, minutely glandular-pubescent, armed at the nodes with pairs of small stipular spines: leaves trifoliate; petioles minutely but densely glandular-pubescent, 1–1½ inches in length; leaflets ovate-lanceolate or narrowly rhombic, mostly acute or acuminate at the apex, acute at the base, puberulent under a lens and minutely ciliate, 1–1½ inches long, 5–8 lines broad: floral leaves numerous, simple, lanceolate or ovate-lanceolate, subsessile, 4–6 lines in length: peduncles slightly puberulent or smooth, about 9 lines long: sepals linear-subulate, acute, reflexed during anthesis: petals spatulate, white, 5 lines in length, the blade about equalling the slender claw: stamens variable, sometimes very unequal in the same flower, some or all of them much exceeding the petals: stipe of the ovary 6–10 lines long; capsule linear, pointed at each end, moderately curved, smooth, but with a fine longitudinal striation, 1¼–1½ inches in length, 1½–2 lines in thickness: seeds striate and muricate.—Tamasopo Cañon, San Luis Potosi, June, 1890 (n. 3538). Near the South American *C. diffusa*, DC., but distinguished by the long stipe of the ovary, slender-clawed petals, long stamens, and longer linear pods. It is also near *C. aculeata*, L., but is amply distinguished by its long-stiped ovary and much exserted stamens.

VIOLA REPTANS. Rhizome short, bearing long fibrous roots: stems numerous, glabrous, prostrate, 6–10 inches long, rooting at the nodes: radical leaves broadly ovate, suborbicular, obtuse or rounded at the apex, cordate, regularly crenate-serrate, smooth on both sides, slightly ciliate on the margin, white-punctate above, paler beneath, 1½ inches long, 1¼ inches broad; petioles 1-3 inches long, pubescent on the upper surface; cauline leaves smaller, ovate, subcordate, more inclined to be pointed: stipules narrow, either subentire or cleft into 2-3 linear acuminate segments: peduncles glabrous: sepals lance-oblong, obtuse or acutish: petals white lined with blue, smooth: valves of the mature capsule 4 lines long, twice the length of the sepals: seeds dark, smooth, and shining. — Hills of Patzcuaro, Michoacan, November, 1890 (n. 3591).

XYLOSMA PRINGLEI, Rob. (P. A. A., XXVI. 164). Additional specimens of this species collected at Las Canoas, San Luis Potosi, June and July, 1891 (n. 3727), give the following supplementary characters. The mature (?) fruit red, spherical, 2 lines in diameter, slightly elevated in the spreading calyx, crowned with the short styles, 1-2 seeded.

KOSTELETZKYA DIGITATA, Gray. Mr. Pringle's no. 3622, from Tamasopo Cañon, San Luis Potosi, collected in June, 1890, appears identical with the type of this species discovered by Dr. Palmer on the Yaqui River, Sonora, 1869. Mr. Pringle's specimen shows the plant to be erect and over two feet in height. The cauline leaves are divided into three linear-oblong, subequal lobes, and have in addition two smaller auricles at the base; the leaves of the branches are simply linear, or have auricles of varying length at the base. The flowers in a dried state appear to be white with a yellow tint.

CASIMIROA EDULIS, Llav. & Lex. Mr. Pringle's no. 3861, from near Guadalajara, represents a form of this species with rather narrow sessile leaflets but three in number.

ÆSCHYNOMENE PETRÆA. A tall erect annual, 4-5 feet in height: stem subsimple, slender, finely striate, nearly smooth: leaves alternate, appressed-silky especially when young, 2-3 inches long; leaflets 15-25 pairs and an odd one, oblong, obtuse, sharply mucronate, 3-4 lines in length: stipules linear, very acute, 1-3 lines long: inflorescence subterminal or the flowers crowded on short, very glandular-pubescent lateral axes; bracts very small, ovate, acute, very pubescent, deciduous: pedicels short, 2-3 lines in length, they and the calyx glandular-pubescent or hirsute: corolla yellow, striped with purple: pod stiped, very deeply parted into 2-4 almost semicircular segments, pubescent especially on the edges and at the nodes; segments thin, flat, 3 lines in diameter, somewhat veiny, but the veins not prominent. — Rocky hills near

Guadalajara, May, 1891 (n. 5147). I am indebted to Mr. Hemsley for the information that this plant is distinct from *Æ. conferta*, Benth., and that it appears to be the same species as Seemann's 2189, collected in the Sierra Madre. In the Gray Herbarium there is a similar plant collected by Seemann in the Sierra Madre, and probably representing his 2189. It certainly seems to be specifically the same as Mr. Pringle's plant, although it represents a somewhat different stage of growth. In it the leaves arise from the stem, and the inflorescence is hirsute and less glandular. In Mr. Pringle's plants the stem-leaves have all fallen, and the entire foliage is crowded upon short secondary axes, giving the specimens a rather different habit.

VIGNA LUTEOLA, Benth., var. ANGUSTIFOLIA. Stem appressed-pubescent: leaflets lance-linear, rounded at the base, 1½–2 inches long, about 3 lines broad: petioles short, not an inch in length.— Wet places near Guadalajara, May, 1890 (n. 3488).

VIGNA STROBILOPHORA. Stem slender, flexuous, branched, covered with a fine soft pubescence: leaves pinnately trifoliate; leaflets ovate, acuminate, entire, rounded at the base, pubescent or glabrate above, somewhat paler and soft-pubescent beneath, 2½ inches long, half as broad; common petioles pubescent, 1½ inches in length: peduncles axillary, rather stout, curved, bearing the flowers in dense racemes: bracts large, ovate, sharply acuminate, entire, scarious, finely striate, somewhat pubescent and ciliated toward the apex, closely imbricated over the buds, deciduous: pedicels single, silky-pubescent, 1–3 lines long: calyx campanulate, short, colored; teeth short and obtuse: corolla blue-purple, 6–7 lines in length; standard orbicular, slightly retuse, with two scale-like appendages at the base; wings bluntly auriculate on the upper side; keel bent nearly at right angles, the end then conspicuously curved inward: stamens diadelphous: style bearded on the outer side near the end; stigma somewhat oblique. — Bluffs of barranca near Guadalajara, September, 1891 (n. 5163). This species is strongly characterized by its large closely imbricated bracts. In its keel it is almost intermediate between Phaseolus and Vigna.

CÆSALPINIA MULTIFLORA. A medium-sized tree, minutely sericeous on the younger parts: foliage and racemes crowded near the ends of the branches; leaves 7 inches or more in length, bipinnate; pinnæ about 10 pairs; common petiole striate-sulcate, 3 inches long; leaflets 15–18 pairs, elliptic-oblong, mucronate, entire, moderately oblique at the base, 4–6 lines in length, 1½–2 lines in breadth, paler beneath: racemes numerous, many-flowered, 6 inches or more in length, flowering from near the base: flowers early deciduous, leaving the rhachis naked below: pedicels 4–5 lines long, articulated somewhat above the middle: calyx-teeth subequal, ovate-oblong, smooth, yellowish brown, subcoriaceous, distinctly but narrowly imbricated, 2–2½ lines long, reflexed in anthesis: petals bright yellow, obovate, erose, 4–5 lines long, one of them with a slightly narrower blade and broader claw, and bearing a small crest-like appendage on the inside near the base: stamens erect, equalling the corolla; filaments silky near the base; ovary hirsute, about 6-ovuled: fruit not seen.— Volcanic hills, Monte Leon Pass, Michoacan, May, 1891 (n. 3730). The very narrow *imbrication of the sepals tends to connect Cæsalpinia and* Poinciana.

LOPEZIA ANGUSTIFOLIA. Somewhat woody near the base: stem purplish, nearly smooth, 2–4 feet high, giving off numerous slender spreading subsimple branches: cauline leaves not persistent, the lower not seen, the upper ones and those of the branches narrowly lanceolate, irregularly subserrate, glabrous, 5–10 lines long, 1–2 lines broad, pellucid-punctate, narrowed to a bluntish point, contracted at the base to a slender petiole (1½–3 lines in length), midrib often reddish: racemes numerous, terminating the stem and branches, not distinctly pedunculate; pedicels not exceeding 6 lines: calyx segments red, linear, narrowed to an obtuse point, the lowest somewhat broader: petals purple, the lower ones obovate, cuneate, 3 lines long, the upper with a linear-oblong blade, scarcely at all auriculate at the base; glands single, very slightly contracted in the middle: sterile stamen with filament not equaling the suborbicular retuse bright-red blade: fruit spherical, 2 lines in diameter.— Limestone ledges of Las Canoas, San Luis Potosi, October, 1891 (n. 3990).

COULTEROPHYTUM, n. gen. of the Umbelliferæ (Selineæ). Stylopodium slender, conical; margin not distinctly undulate. Fruit clavate, subterete in cross-section, contracted below the seeds into a short winged stipe-like base; commissure broad; carpels compressed dorsally; the primary ribs narrowly winged, the lateral wings slightly broader; oil-tubes single at the intervals, about four on the commissure; seed-face concave.— Tall perennial of robust habit; leaves bi- or tripinnate: inflorescence much branched; umbels compound: bracts of the involucres and involucels several, small, filiform. This genus appears most closely related to Ligusticum, differing from it chiefly in the more slender conical stylopodia, solitary oil-tubes, carpels dorsally flattened, and fruit contracted below. In its habit and lax inflorescence it somewhat resembles Arracacia, but its much broader commissure and the form of the seed would place it rather among the Selineæ. I take pleasure in dedicating the genus, at the desire of the discoverer, to Professor John M. Coulter, who with Mr. J N. Rose has so carefully elaborated the North American species of this difficult order. To Mr. Rose I am indebted for kind assistance in determining the generic affinities of the plant here described.

C. LAXUM. Stem somewhat woody, 5–10 feet high, an inch in thickness, with prominent nodes: leaves bi- or tripinnate, 18 inches in length, with enlarged sheathing petioles; leaflets ovate or ovate-lanceolate, serrate, acuminate at the apex, rounded at the base, almost smooth above, pubescent on the veins beneath with minute stiff hairs: inflorescence lax, several times branched, branches bearing compound umbels with 6–12 rays: bracts of the involucre 1–4, sometimes wanting, short, filiform; bractlets similar, usually more numerous: fruit 4 lines long; the contracted base a line in length: flowers not seen. — Bluffs of barranca near Guadalajara, September, 1891 (n. 3831).

OLDENLANDIA PRINGLEI. Cæspitose: stems ascending or prostrate, subsimple or considerably branched, usually springing from elongated scaly rhizomes: leaves pseudo-verticellate, in groups of 4–8, linear, acute, appearing somewhat fleshy: flowers borne in rather loose terminal cymes: pedicels 1–3 lines in length: corolla salver-formed, 4-lobed, 2–2½ lines long, purple in a dried state: stamens and pistil dimorphous; anthers either inserted on the middle of the tube or just exserted from its summit: ovary entirely inferior, crowned in fruit by the lanceolate approximate calyx teeth; these almost equalling the capsule in length: seeds smooth, numerous, obtusely angulate, not concave.— Alkaline plains, Hacienda de Angostura, San Luis Potosi, June, 1891 (n. 3758). A plant of almost equal affinity to Oldenlandia and Houstonia, possessing the numerous small angulate smoothish seeds and entirely inferior ovary of the former, but the dimorphous flowers and linear anthers of the latter.

CRUSEA MEGALOCARPA, Wats. (P. A. A., XXVI. 137), *Spermacoce megalocarpa*, Gray (Ibid., XXI. 381). Mr. Pringle's specimens of this species being in flower, the floral characters which seem never to have been described, may now be given. Corolla smooth and (in a dried state) purplish-blue, 6 lines long; tube very slender; limb of 4 linear-oblong lobes, spreading or moderately reflexed: stamens and pistil conspicuously exserted, anthers blue, curved, versatile.— On dry talus of cliffs in shade, barranca near Guadalajara, September, 1891 (n. 3852). The elongated corolla fully confirms Dr. Watson's view that this is a Crusea, and not a Spermacoce.

VALERIANA ALBONERVATA. Tuber two inches in diameter: stem erect, two feet in height, sulcate-striate, pubescent, subsimple up to the branched inflorescence, nearly leafless: radical leaves numerous, pinnate; leaflets 3–4 pairs and an odd one, broadly obovate or suborbicular in outline, sometimes an inch in diameter, mostly smaller, cuneate at the base; limb more or less divided into 3–5 broad rounded lobes; the edges and veins beneath covered with a short and dense white pubescence: petioles pubescent, 2–4 inches long; cauline leaves 1–2 pairs, distant, much reduced: inflorescence regularly dichotomous; bracts awl-shaped, 1–1½ lines long: flowers small; corolla a line wide, scarcely half as long: stamens exserted: fruit ovate, glabrous, 2 lines long, crowned by the spreading plumose calyx-teeth of the same length. — Hillsides, San José Pass, San Luis Potosi, July, 1890 (n. 3612).

EUPATORIUM FILICAULE, Schultz Bipontinus. Stem slender, terete, striate, the upper part covered with a very short close pubescence: leaves opposite, membranaceous, petiolate, ovate, sharply acuminate, subcordate or somewhat hastate, serrate, nearly or quite glabrous on both surfaces, 2 inches long, 1¼ inches wide: petioles flexuous, pubescent, 9 lines or more in length: inflorescence of slender opposite spreading branches, bearing numerous sub-racemose heads: pedicels filiform, 1–1½ lines long, fasciculately grouped upon the branches: bracts filiform: heads 2½ lines long: scales of the involucre 9–12, linear-oblong, sharply acuminate, the two or three outermost much shorter than the others, all thin, striate, tending to turn purple, minutely pulverulent-pubescent: achenes somewhat clavate, puberulent at the angles, narrowed below into a sort of stipe.— Near *E. Palmeri*, Gray, but differing in its more delicate foliage, more racemose heads, and in the achenes attenuated downward. This and the following seem to be good species, which were named by Schultz Bipontinus, but, so far as I have yet been able to learn, were never described. The description above is drawn, not from the type which is Ehrenberg's no. 1176 (in the Berlin Herbarium), but from a specimen collected by Schaffner in Orizaba, October, 1855. The latter plant was identified with Ehrenberg's by Schultz himself, who employed the ! sign to express special definiteness. Bilimek's no. 576, Orizaba, May, 1867, and Bourgeau's 1703, Valley of Cordova, January, 1866, have been identified with this species by Dr. Gray. Mr. Pringle's plants collected on ledges of the Tamasopo Cañon, November and December, 1890 (nos. 3649 and 3956), are also certainly to be referred here, although the leaves are more deeply hastate.

EUPATORIUM SCHAFFNERI, Schultz Bip. Root a cluster of thickened fibres: stems 2–3, terete, pubescent, tending to turn dark purple, a foot or two in height, sparingly branched: leaves opposite, petiolate, ovate, crenate-serrate, acutish, truncate at the base, subglabrous, 1¼ inches long, an inch wide: petioles 4–7 lines in length, the upper shorter: heads corymbose, pedicellate, about 25-flowered, 1½ lines long (somewhat immature): scales of the involucre equal, obtusish or more or less pointed, thin, sub-transparent, but with 2–3 strong nerves in the middle near the base: achenes immature.— Description drawn from the type collected by Schaffner in Mexico near S. Angelos, 1855 (n. 28). In the Gray Herbarium the following specimens may be referred to this species: Schaffner's no. 292 ex convalli San Luis Potosi, August, 1876; Parry and Palmer's 345, from a similar locality, 1878; and Pringle's 3662, Flor de Maria, Mexico, October, 1890. These specimens, which are more mature than the type, show the heads to be a trifle larger, the ripe achenes to be small, dark, scarcely contracted below, puberulent both on and between the angles.

EUPATORIUM LEMMONI. Stoloniferous: stems subsimple or much branched, terete, dark purple, with close white pubescence: leaves all opposite, sessile, mostly elliptic or ovate-elliptic, obtusish, 10–14 lines long, about half as wide, crenate-serrate (sometimes obsoletely so), glabrous above, sparingly pubescent upon the veins beneath: the lower leaves smaller, rounder; the uppermost more ovate and acute: heads 3½ lines high, on peduncles half an inch in length: the sharply pointed nearly smooth scales of the involucre subequal: flowers rather numerous; corollas white; achenes somewhat puberulent.— First collected by Mr. J. G. Lemmon in the Chiricahua Mountains of Southern Arizona, 1881 (n. 316 in part); then by Dr. Edward Palmer in Southwestern Chihuahua, August to November, 1885 (n. 332); and by Mr. Pringle on cool rocky slopes of the Sierra Madre, September, 1887

(n. 1264). Mr. Lemmon's specimens were supposed by Dr. Gray to belong to *E. Rothrockii*, with which they had been associated, and it is to them that he referred (Syn. Fl. I. 2. 102) in speaking of depauperate forms of *E. Rothrockii* with sessile leaves.

XANTHOCEPHALUM TOMENTELLUM. Perennial, 2–3 feet high: stem simple, leafy up to the corymbose inflorescence, striate, tomentulose: leaves entire, thickish, pale green, glabrate above, tomentulose beneath; the radical ones oblanceolate or spatulate, rounded at the apex or obtusely pointed, 2–2½ inches in length, narrowed at the base to petioles 3–4 inches long; the cauline oblanceolate; the lower contracted below into broad more or less clasping petioles; the upper sessile, acute: branches of the inflorescence angulate, bearing the heads in rather dense terminal corymbose groups: heads 2½–3 lines long, about as broad; involucre campanulate; scales regularly imbricated in several rows, abruptly pointed, the scarcely thickened ends appressed or slightly spreading: rays numerous, not exceeding the disk flowers: pappus in both ray and disk flowers a crown of short unequal scales more or less united into a cup; achenes glabrous, 2-edged, with or without one or two intermediate angles.— Alkaline meadows, Hacienda de Angostura, San Luis Potosi, July, 1891 (n. 3761).

BELLIS PURPURASCENS. Perennial: root of numerous fibres: stem procumbent, much branched, angulate, striate, covered with spreading white pubescence: branches simple or again divided, terminating in long slender simple peduncles: leaves elliptic lanceolate or the lower somewhat spatulate, acute or acutish, entire, sessile tending to turn purple, 8–18 lines long, 3–5 lines broad, pubescent on both sides and ciliate: heads including the rays 7–8 lines in diameter: involucre spreading, the bracts in two series, lanceolate, acuminate, herbaceous in the middle, with margins somewhat scarious (not so distinctly so as in *B. integrifolia*): rays purplish white: disk deep yellow.— Shaded grassy slopes, barranca of Las Canoas, San Luis Potosi, August, 1891 (n. 3819). This plant was distributed as *B. xanthocomoides*, Gray (*Brachycome xanthocomoides*, Less.), the material of that species in the Gray Herbarium being insufficient to prove the distinctness of Mr. Pringle's plant. I am indebted to Prof. N. L. Britton for definite information on the subject, and for the kind loan of Schiede's no. 206 from the Herbarium of Columbia College, which shows *B. xanthocomoides* to be certainly distinct, differing in its much less robust and branching habit, its solitary heads, long slender runners, more decidedly spatulate leaves, and the absence of the coarse spreading pubescence.

ERIGERON HETEROMORPHUS. Amphibious, glabrous throughout: stems dark-colored, subsimple, rooting for some distance along a decumbent base: leaves of two very distinct forms, those of the terrestrial specimens three-lobed to the middle, sessile by a cuneate base, 2 inches long, an inch or more broad; the lobes laciniately cleft: leaves of the sterile aquatic stems linear, elongated, subentire or more or less divided, 4 inches or more in length: heads including the rays 7–8 lines in diameter, borne singly on peduncles 3–4 inches in length: involucre of subequal moderately imbricated flat smooth green subulate scales with very narrow scarious margins: rays about 50, narrow, pure white.— Growing from calcareous tufa, more or less submerged, Cascades of the Concepcion River near Micos, San Luis Potosi, December, 1891 (n. 3963). A remarkable species near *E. scaposus*, DC., but strongly characterized as well by the smooth green scales of its involucre as by the presence of the floating leaves.

MELAMPODIUM LONGIPILUM. A span or more high, cymosely branched almost from the base: stem rather stout, the young internodes white with soft long spreading hairs, the older parts pilose but much less densely so: leaves ovate or somewhat rhombic, obtuse or rarely acute, contracted at the base and narrowly connate, entire, appressed-pubescent, punctate, 2–2½ inches long, half as wide: peduncles slender, very pubescent: bracts of the involucre distinct, obovate, pointed, hirsute over the whole outer surface: rays about 10, deep yellow, 2–3 lines in length: fertile bracts laterally tuberculate-roughened, bearing a small acuminate recurved appendage at the summit: disk somewhat elevated in the centre.— San José Pass, San Luis Potosi, July, 1890 (n. 3639). This plant stands very near *M. divaricatum*, DC., of which it may possibly prove to be a well marked variety. It differs, however, in its very hairy stem, and in its involucral bracts, which are not only narrower and more acute, but are pubescent-hirsute over the entire outer surface, instead of being merely ciliate, as in *M. divaricatum*. Furthermore, the leaves are entire and incline to be more obtuse, while the fertile bracts are very tuberculate and are provided with longer appendages.

SABAZIA MICHOACANA. Perennial, 2–3 feet high: stem slender, purple, hirsute-pubescent, somewhat branched, springing from a short horizontal rootstock: leaves opposite, ovate-lanceolate, serrate, acute at the apex, obtusish at the base, more or less distinctly 3-nerved, pubescent above, canescent-tomentose over the whole surface beneath, 1½–2 inches long, 7–9 lines broad: petioles short, pubescent; bracts of the loose corymbose inflorescence small, lance-linear, 3–4 lines long: heads about a dozen, including rays 6–8 inches in diameter: scales of the involucre ovate, acute, the outer somewhat shorter, the inner longer, narrower, more oblong and more acute, but scarcely acuminate: rays about 10, white, tube hirsute-pubescent, ligula broadly elliptic, 3-toothed, 3 lines long: disk flowers yellowish white (?), tube hirsute-pubescent, limb 5-toothed: anthers entire at the base: style tips with short blunt appendages: achenes small, black, oblanceolate in outline, hispidulous: pappus none. — Mountains near Patzcuaro, Michoacan, November, 1891 (n. 4099). Distinguished from *S. Liebmanni*, Schultz Bip. ex char.,* by having heads loosely corymbose, not solitary, leaves ovate-lanceolate not elliptic, tomentose over whole surface beneath instead of along the nerves.

GYMNOLOMIA CANESCENS. Stem striate-furrowed, branched, leafy below, nearly leafless above, clothed with a close gray more or less deciduous pubescence, and sparingly villous: leaves opposite, ovate, subcordate, entire, acute or obtuse, triply nerved, 2–3½ inches long, roughish-pubescent above, canescent beneath with silky appressed hairs; petioles 6–8 lines long: inflorescence of several slender naked branches, each bearing 1–8 rather closely aggregated heads (4–5 lines in diameter): pedicels and bracts of the involucre canescent, the latter lanceolate, acuminate, rather loosely imbricated in 2–3 series, the outer somewhat shorter: rays 5–7, yellow, not exceeding the disk: chaff ovate-lanceolate, carinate, terminating in acute pubescent points, with or without lateral teeth: style branches of the disk flowers with rather attenuated tips: achenes dark, mottled with light color: pappus none. — Brackish marsh, Las Tablas, San Luis Potosi, June, 1890 (n. 3611), and alkaline plains, Hacienda de Angostura, San Luis Potosi, June, 1891 (n. 3763). This species differs from the other Gymnolomias which I have examined, in having more attenuated style tips, but it appears better placed in this genus than elsewhere.

TITHONIA BRACHYPAPPA. Stem terete, striate, smooth or nearly so, branched above: branches terminating in peduncles thickened upward and subscabrous; cauline leaves alternate, 2–2½ inches in diameter, deeply 3-lobed, broadly cordate, scabrous above, pubescent beneath, lobes serrate, acuminate, the middle one more or less panduriform: petioles 9 lines long, winged: wings decurrent for some distance upon the stem: heads exclusive of the rays an inch in diameter: involucre hemispherical; bracts striate, with subfoliaceous tips, the outer shorter, rounded at the apex, the inner equalling or slightly surpassing the disk, acute: rays about 8–10, deep yellow, 9 lines long; chaff scarious, carinate, very sharply acuminate, with or without lateral teeth: achenes 4-angled but decidedly compressed, narrowed downward, dark in color, often mottled with light red: pappus none or in the same head consisting of a ring of short unequal rather rigid teeth.— Las Palmas, San Luis Potosi, October, 1890 (n. 3675). This plant has so perfectly the habit and characters of a Tithonia that it should certainly be referred to this genus notwithstanding its short sometimes obsolete pappus. From *T. tagetiflora*, Desv., it differs in its involucre; from *T. diversifolia*, Gray, in its considerably smaller heads and shorter rays, as well as in achenes and pappus.

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* Klatt in Leopoldina, XXIII. 2.

VERBESINA POTOSINA. Stem rather stout, furrowed, pubescent, leafy to the summit: leaves alternate, lance-oblong, attenuate, acute, sessile, auriculate, denticulate on the subrevolute edges, roughish pubescent above and finely dotted with the enlarged white bases of the hairs; white tomentose beneath, less so on the veins: heads rather numerous, 5–6 lines in diameter, loosely corymbose, peduncles pubescent, 1–3 inches in length: scales of the involucre lanceolate, sharply acuminate, canescent, rather loosely imbricated, not equalling the disk flowers; rays about 12, very small, scarcely exceeding the involucre, yellow: disk strongly convex: chaff scarious, keeled, pubescent near the acuminate tips: disk flowers deep yellow: achenes oblanceolate, 1½ lines in length, notched at the summit and with a slight angle on each face; wings moderately broad, upwardly ciliate, subacute above. — Mesas, Hacienda de Angostura, San Luis Potosi, July, 1891 (n. 5113). Near *V. auriculata*, DC. (ex char.), but differing in its radiate heads, narrower leaves, and lanceolate acuminate involucral scales.

VERBESINA PRINGLEI. Fruticose: branches covered with a whitish cortex; branchlets strongly angled, glabrous or nearly so: leaves opposite, lanceolate, attenuate, acute, rather coarsely and irregularly serrate-dentate, of harsh texture, scabrous above, pubescent but scarcely rough beneath, 3–5 inches long, 1–1½ inches wide, narrowed below to short petioles: cymes few-headed, scarcely or not at all exceeding the upper leaves: pedicels ½–1 inch in length, pubescent: heads discoid, orange-yellow, 5 lines high, about 12-flowered: bracts of the involucre about 10, the outer oblong or spatulate, obtuse, scarcely half the length of the flowers, the inner more or less acute: corolla hispidulous upon the outer surface: achenes black, with broad wings and two nearly erect awns: heads of fruit subglobose: the plicate chaff with bright yellow curved tips exceeding the achenes. — Dry rocky bluffs of barranca near Guadalajara, September, 1891 (n. 3845). This species differs from *V. serrata*, Cav., in its shrubby habit, narrower leaves, somewhat smoother stem, etc. Berlandier's no. 1289, collected at Monte San Juan del Rio, November, 1827, is evidently nearly related to Mr. Pringle's plant, but the specimen is too fragmentary for certain identification; there appear to be slight differences in the achenes, and the heads of Berlandier's plant do not have the chaff conspicuously curled in fruit.

SPILANTHES BECCABUNGA, DC., var. PARVULA. Root a cluster of thickened fibres: stems several, decumbent, 4–6 inches high, rooting at the lower joints: leaves ovate, entire, including petiole only 6–10 lines long, half as broad: heads a little smaller and rays shorter than in the typical form: anthers dark, slightly caudate at the base. — Wet soil, Flor de Maria, State of Mexico, August, 1890 (n. 3643). This may perhaps be a distinct species.

SPILANTHES DISCIFORMIS. Stem prostrate, woody, verrucose, rooting at the joints, and sending up numerous subsimple, more or less fleshy, glabrous, purplish branches: leaves lance-oblong or lance-linear, triply-nerved, entire, glabrous, 10–14 lines long, 1½–3 lines wide, usually considerably exceeding the internodes, narrowed to a blunt point, contracted below to a short, sometimes ciliated petiole: peduncles at the ends of the branches, striate, glabrous, 2 inches long: scales of the involucre ovate (not lanceolate nor oblong), acute, subciliate: rays yellow, inconspicuous, scarcely exceeding the involucre, the heads at first sight thus appearing discoid: receptacle much elevated: disk flowers yellow: anthers entire at the base: achenes black, ciliate at the angles, and slightly hispid on the faces, exaristate. — Wet meadows, near Guadalajara, May, 1890 (n. 3489). A stout, somewhat fleshy species, differing from *S. Beccabunga* in its more woody stem, narrower entire leaves, shorter rays, ovate scales, and entire anthers.

LEPTOSYNE PINNATA. Acaulescent: root of several thickened fibres: the base of the plant covered with brown wool, as in some species of Cacalia: leaves including petioles a foot in length, pinnate, glabrous; leaflets 4–6 pairs and an odd one, elliptic-lanceolate, acute at each end; the terminal one much larger, 8–10 lines long, obscurely crenate, with minute glands in the sinuses of the crenation; scapes a foot high, simple or branched, bearing one or more linear bracts: involucre double, the outer bracts narrowly oblong, exceeding the broader inner ones, all obtuse: heads solitary, exclusive of the rays ½ inch in diameter: rays white, 4–5 lines long, fertile: disk flowers yellow, their corollas destitute of an annulus at the junction of the tube and throat: achenes slightly ciliate on or near the summit, but without a distinct pappus. — Wet meadows, Del Rio, State of Mexico, August, 1890 (n. 3668). This plant approaches most nearly the genus Leptosyne, differing from it, as heretofore limited, chiefly in its white rays and in the absence of an annulus on the disk corollas. The neighboring genera, Dahlia and Bidens, show, however, what variation is to be expected in the color of the rays, and in *L. Mexicana*, Gray, which Dr. Gray pronounces a good Leptosyne, there is scarcely a trace of an annulus. Mr. Pringle's plant is certainly very distinct in its habit from any known species of the genus.

GEISSOLEPIS, n. gen. of the Compositæ (Galinsogeæ). Heads heterogamous, radiate. Flowers all fertile, rays white, disk yellow. Involucre turbinate-campanulate; scales ovate, obtuse, closely imbricated in 4–5 rows, the outer regularly shorter. Receptacle chaffy in all parts, but not alveolate; chaff obovate, obtuse, ciliate. Disk flowers regularly 5-toothed, throat not enlarged. Anthers entire below. Style divided nearly to the middle; the branches flattened, bearing short conical appendages. Achenes 4-angled, pubescent, crowned with 7–8 very acute awl-shaped, minutely and retrorsely ciliated scales. — A prostrate, somewhat succulent herb, with alternate entire linear leaves: heads small, solitary on lateral peduncles arising opposite the leaves. This genus is perhaps best placed just before Blepharipappus. The generic name, derived from γεῖσσον and λεπίς, has reference to the well imbricated scales of the involucre, one of the distinctive characters of the genus.

G. SUÆDÆFOLIA. Stems prostrate, giving off numerous subsimple branches: branches 4–6 lines in length, finely pubescent, especially at the nodes: leaves glabrous, fleshy, 6–8 lines long, half a line in breadth, sessile: heads including rays 8 lines in diameter; rays elliptic, 3-toothed, 2–3 lines in length. — Alkaline plains, Hacienda de Angostura, San Luis Potosi, June, 1891 (n. 3762).

FLAVERIA ANOMALA. A glabrous annual, a span high: stem striate-angulate, much branched: leaves linear or lance-linear, gradually narrowed to a slightly connate base, acute, 1½–2 inches long, 1½–2½ lines wide: heads numerous, aggregated at the ends of the branches in dense corymbs, very small, subtended by minute dark-tipped bracts, 1- (rarely 2-) flowered; the single flower either tubular or ligulate: involucral scales of unequal breadth, lance-linear or oblong, more or less narrowed but obtuse at the apex, persisting in fruit and becoming swollen and bulbous on the back near the base: corollas bright yellow; in the tubular flowers the campanulate throat and spreading limb equalling the tube, the latter hairy on the outer surface; the ligules a line or less in length: achenes oblanceolate, ribbed, black. — Plains, Vanegas, San Luis Potosi, September, 1890 (n. 3669). This interesting plant was first collected by Dr. C. C. Parry in Northern Mexico, 1878 (n. 31), and again the same year *en route* from San Luis Potosi to San Antonio, Texas (n. 500); but Dr. Parry's specimens were determined (probably by Mr. Hemsley) as *F. linearis*, Lag. "forma morbida." Dr. Gray noted the specimens as a new species, but appears never to have described them. Mr. Pringle's plants, collected twelve years later and agreeing closely with Dr. Parry's, seem to show that they represent a permanent species, and not merely a casual form. In its very few-flowered heads this species approaches *F. repanda*, Lag.

POROPHYLLUM PRINGLEI. A smooth pruinose annual, 1½–2 feet in height: stem terete, simple below, branching above: leaves elliptic, subentire, with rounded apex and acute base, delicate in texture; the cauline mostly opposite, 1–2 inches long, half as broad, on slender petioles of nearly equal length; the rameal mostly smaller, inclining to be alternate: glands of the leaves few, all marginal, broadly elliptic, light brown: heads rather few, scattered, 9 lines in length, tapering and very acute in bud: scales of the involucre narrow, ¾ of a line in breadth, acuminate, with scarious margins and a single median row of glands: peduncles arising singly: flowers few, about 12, little or not at all exceeding the involucre: corolla tube very slender, about equalling the achene in length; the limb very small, nearly white. — Barranca near Guadalajara, September, 1889 (n. 2954); also in a similar locality, October, 1891 (n. 5168). This species is near *P. Ervendbergii*, Gray, but differs in its scattered, not at all cymose heads, and larger, thinner entire leaves glandular only on the margins.

CNICUS EXCELSIOR. Very tall, 6–10 feet high: stem ribbed, partially covered with a deciduous arachnoid pubescence: lower leaves lanceolate, acute, subentire, somewhat repand toward the base, spinulose-ciliate, 8 inches long, 2 inches broad, narrowed below into a petiole 2–3 inches in length, pale green and more or less arachnoid above, covered beneath with a thin gray arachnoid tomentum; cauline leaves sometimes a foot or more in length and 5 inches in breadth, sinuate-pinnatifid, with triangular, acute lobes, spinulose on the edges, sessile and conspicuously decurrent in broad wings (3–4 inches in length): inflorescence branching; the branches bearing toward their summits several small rather closely aggregated heads: heads in anthesis 7–8 lines, in fruit 1 inch broad; scales of the involucre appressed, regularly imbricated, narrowly ovate, narrowed above or somewhat abruptly contracted to a short ascending or spreading yellowish spine, and bearing near the apex just beneath the spine a dark glandular (?) streak; the inner bracts longer, narrower, very acute but unarmed, purplish: corollas purple, the narrow throat contracted very gradually into the slender tube; limb not very oblique: filaments hairy: style branches short, not exceeding ¾ of a line in length; annulus inconspicuous. — Among shrubs, low lands, Hacienda de Angostura, July, 1891 (n. 3768). Near *C. altissimus*, Willd., which it resembles in its soft, weakly armed leaves of varying form, closely also in its involucre and the color of its flowers, as well as in its tall habit. It differs, however, in its strongly decurrent leaves, smaller, more numerous, and closely aggregated heads, shorter style branches, and less oblique corolla.

PEREZIA MICHOACANA. Stem slender, striate-angulate, glabrous, dark purple, 4–6 feet in height, bearing a loosely corymbose, rather few-headed inflorescence: leaves obovate-spatulate, sharply denticulate, rounded at the apex, auriculate-clasping at the base, glabrous, veiny, thickish, and somewhat rigid; the lower ones 6 inches long, half as broad; the upper smaller and more inclined to be acute; those of the inflorescence much reduced, 3–9 lines in length, linear-oblong, acute: heads ¾ of an inch high, 40-flowered: scales of the involucre dark purple, fulvous-tomentose on the edges, imbricated in 5–6 ranks and varying greatly in length, the outer being very short, but all acute: corolla purplish: style branches recurved: immature achenes linear, striate, glandular-roughened. — Hills near Patzcuaro, Michoacan, December, 1891 (n. 3988). This species stands near *P. rigida*, Gray, but differs from it in its more numerously flowered heads, in the character of the involucre, and somewhat in the shape of the leaves. The heads, however, are not so large as in *P. formosa*, Gray, and *P. turbinata*, Llav. & Lex., nor do the involucral bracts extend down upon the peduncles as in these species.

ANDROSACE (?) CINERASCENS. A spreading perennial of grayish green color, 6–10 inches in height, a little woody at the base: stems ascending, several times branched, very leafy: leaves narrowly linear, acute, sessile, perhaps slightly fleshy, 1–1½ inches long, ½–¾ of a line broad: peduncles slender, smooth, 3–4 inches long, bearing 4–8 corymbosely grouped flowers; pedicels ebracteolate, filiform, 6–8 lines long: the short calyx tube hemispherical; segments lanceolate, acuminate. corolla small, salver-shaped, 2 lines long, white or nearly so: capsule enclosed by the persistent calyx, dehiscent by 5 valves: placenta spherical, raised on a very short stipe: seeds numerous, minute. — Alkaline plains, Hacienda de Angostura, San Luis Potosi, July, 1891 (n. 3765). This plant, which is very different in habit and inflorescence from any Androsace which I know, appears nevertheless to agree with that genus in all essential characters of flowers and fruit. The genus as described by Bentham and Hooker is rather widely drawn. The species just characterized agrees more nearly with § *Aretia* than with *Euandrosace*, but differs from both in its inflorescence.

DICTYANTHUS TUBEROSUS. Root thickish, enlarged and fusiform toward the end, resembling a small tuber: stem short, somewhat woody, erect or procumbent, bearing near its summit several subsimple spreading hirsute branches: leaves ovate, acuminate, entire, deeply cordate, with a narrow but rounded sinus, pubescent on both surfaces and ciliate, 1–1½ inches long, on hirsute petioles 4–7 lines in length: flowers occasionally solitary, usually 2–4 together, with or without a short common peduncle; pedicels 2–4 lines long: calyx divided nearly to the base into lanceolate acuminate hirsute segments, 3–4½ lines in length: corolla campanulate, 4–6 lines deep: tube marked with narrow purple stripes; limb of spreading triangular segments of dark color, and but 2–3 lines in length: follicle narrowly lanceolate in outline, about 2 inches long, tapering to a bluntish apex, armed with short, firm spines, and appearing striate from numerous minute longitudinal folds of its outer integument. — Slopes of barranca near Guadalajara, September, 1890 (n. 3568). First collected by Dr. Edward Palmer near the same locality, July, 1886 (n. 251). Dr. Palmer's specimen was referred by Dr. Gray (P. A. A., XXII. 436) to *D. stapeliæflorus,* since it accorded with Reichenbach's exceedingly defective description. The additional notes and excellent plate of that species in Regel's *Gartenflora,* Vol. VI., however, show clearly that it is altogether different, with larger, somewhat undulate leaves, much shallower corolla tube, and broader differently colored limb. Mr. Pringle's specimen and one of Dr. Palmer's show no tendency toward a climbing habit; but a detached branch with Dr. Palmer's no. 251 has longer, flexuous internodes, suggestive of such a character. The flowers on this branch are larger, and the common peduncles longer.

GONOLOBUS SUBERIFERUS. Stem covered with a thick rough light yellowish corky bark: branches, petioles, and peduncles covered with a spreading pubescence: leaves ovate, acuminate, deeply cordate, with a narrow, often closed sinus, pubescent on both surfaces and ciliate, 1½–2 inches long, 1 inch broad: petioles an inch long: peduncles about half as long, each bearing a single pedicel an inch in length: calyx segments ovate-oblong, acute, pubescent and finely granular on the outer surface, ciliate, nearly smooth within, corolla 1¼ inches in diameter; segments ovate, obtuse, yellowish green, very minutely granular, otherwise smooth, exceeding the calyx by half, not conspicuously marked or veined: top of column white: crown dark brown: follicles slender, smooth, more than 3 inches in length, the calyx persistent at its base. — San José Pass, San Luis Potosi, July, 1890 (n. 3631).

PHACELIA NAMATOSTYLA. A small, slightly fleshy annual: stems numerous, short, 2–3 inches in length, prostrate, branching, pubescent: leaves bipinnatifid, 8–12 lines in length; pinnæ about seven pairs and terminal one, oblong, obtusely lobed, covered above with a fine gray pubescence, smoothish below, except the midrib; margins strongly revolute: racemes numerous, dense, not exceeding the leaves; bracts minute or obsolete; flowers very small: calyx lobes oblong-spatulate, corolla white, a line in length, campanulate with slightly spreading limb of five rounded lobes: stamens inserted upon the lower part of the tube, scarcely equalling the corolla; filaments smooth: style divided nearly to the base; summit of the ovary pubescent; ovules two on each placenta, pendent; capsule globose, shallowly sulcate in the middle of each of the two valves; seeds dark brown, one line in length, conspicuously pitted. — Carneros Pass, Coahuila, May, 1890 (n. 3493). This species is anomalous in its style, which is divided practically to the base, as in

Nama. Its much divided leaves, however, would not go well in that genus.

CORDIA ALBA, R. & S. Mr. Pringle's specimens of this species, collected at Las Palmas, San Luis Potosi (nos. 3676 and 3754) have light yellow flowers as in Wright's 425 from Cuba and Fendler's 921 from Venezuela. No. 3754 has short stamens and considerably longer styles, thus representing the complementary form to that of Ghiesbrecht's 832 and Wright's 425 with exserted stamens and short styles. Darwin* found the difference in the length of the stamens in an undetermined Cordia very slight, the anthers in both forms being "seated in the mouth of the corolla." Here, however, the difference is very noticeable, the stamens of the short-styled form being considerably exserted from the throat, although not exceeding the limb of the corolla.

LITHOSPERMUM CALCICOLA. A cinereous perennial: a foot or more in height, several-stemmed from a branching distinctly ligneous base: stems covered with a spreading hirsute pubescence, subsimple and naked below, branched and very leafy above: leaves elliptic, obtuse, slightly mucronate, sessile, 12–15 lines long, 3–4 lines broad, appressed-pubescent on both sides, white-punctate above; the upper ones similar but somewhat smaller: flowers very small, subsessile: calyx segments lance-linear, densely hirsute, in anthesis scarcely more than a line in length, in fruit 2–3 lines long: corolla very short, scarcely exceeding the calyx: nutlets ovate, more or less conspicuously keeled on the inner surface, usually only one maturing, dark brown, shining, deeply pitted, becoming nearly 2 lines long. — Limestone ledges, San José Pass, San Luis Potosi, July, 1890 (n. 3529). This plant considerably resembles *L. Matamorense*, DC., but differs in its ligneous distinctly perennial base. Its stems are rather more leafy above, the leaves less contracted at the base, and the nutlets slightly larger.

LITHOSPERMUM REVOLUTUM. Perennial: stems one or several arising from a single thickish root, simple or somewhat branched, pubescent, scabrous: lower leaves falling off; the middle and upper stem-leaves thick, oblong or elliptic, entire, revolute on the edges, rounded at the apex, sessile, very scabrous above, pubescent and scarcely paler beneath, 1–2 inches long, 3–7 lines broad: inflorescence rather dense; bracts ovate, ciliate, acute, 4 lines long, not equalling the calyx lobes; flowers short-pedicelled: calyx lobes linear, nearly equalling the tube of the corolla; the latter apparently yellowish, 4–5 lines in length, with small only slightly spreading limb: style exserted; nutlets small, shining, white or discolored, scarcely keeled. — Alkaline meadows, Hacienda de Angostura, San Luis Potosi, July, 1891 (n. 3802). Distributed as a form of *L. strictum*, Lehm., equalling Schaffner's no. 728. A more careful examination shows that it is not very near Schaffner's doubtful plant, and is certainly distinct from *L. strictum*, which has linear acute leaves, narrow bracts, and keeled nutlets. Mr. Pringle's no. 3245, distributed last year as *L. strictum*, probably also represents a new species. It is much more robust than *L. strictum*, and has a fusiform root more than half an inch in thickness.

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* Different Forms of Flowers, pp. 117, 118 (orig. edit.).

IPOMŒA ORNITHOPODA. Glabrous, stem slender, twining, angulate, dark colored: leaves very deeply palmately or rather subpinnately 5–7 parted; lobes linear, 1½–2 inches long, 1–2 lines broad, obtuse, apiculate, entire or wavy; the edges revolute; petioles 6–8 lines long: peduncles springing from most of the axils, but many of them abortive; the developed ones 2–3 inches long, one-flowered; pedicels ½ inch long, somewhat thickened upward: sepals orbicular, thin, 5–6 lines in diameter, rounded or even retuse at the summit, purplish on the margins: tube of the corolla very short, included in the calyx, limb 1½–2 inches in diameter, with a broad open throat, appressed-villous on the outer surface, color uncertain: fruit not seen. — Hills, Canoas, San Luis Potosi, July, 1890 (n. 3553.)

GERARDIA PUNCTATA, Rob. (P. A. A., XXVI. 172). Additional specimens of this plant, collected at Carneros Pass, Coahuila (n. 3682), and Las Canoas, San Luis Potosi (n. 3938), show that it is probably perennial. The corolla sometimes attains a length of 16 lines. The name was unfortunately chosen, since the punctate character of the calyx appears to be exceptional, and perhaps due to the presence of a fungus. Notwithstanding its seemingly perennial nature and longer flowers, this species may prove to be the *G. dasyantha*, Cham. & Schl., insufficiently characterized in Linnæa, V. 104, and DC. Prod., X. 517.

BELOPERONE FRAGILIS. Stem 3–5 feet high, somewhat branched, smooth, scarcely striate, strongly contracted above the nodes and readily disarticulating in a dried state; the transverse lines connecting the bases of the petioles often bearing a tuft of hairs, especially in the younger parts of the plant: leaves ovate, acuminate, blunt at the apex, obtuse or rounded at the base, 1½–3 inches long, nearly half as broad, minutely pubescent above, nearly smooth below, only the axils of the veins bearing tufts of white hairs: petioles ½–1 inch long: inflorescences axillary, opposite, racemose; bracts few, small, lanceolate; bractlets minute, subulate; calyx glandular-pubescent, of five lance-linear segments, 2 lines long: corolla pubescent on the outer surface, reddish, strongly veined, nearly an inch long; tube narrow; lips subequal, the upper erect, emarginate, the lower spreading, with three very shallow rounded lobes: stamens close to the upper lip, inserted rather low down on the tube; anther cells nearly equal in size, one inserted higher than the other and oblique, both with a small white spur at the base: fruit not seen. — Limestone ledges, Las Canoas, San Luis Potosi, October and December, 1891 (n. 3933).

Habenaria Pringlei. Roots mostly fibrous, but the central one tuberous: stem 3 feet high: leaves sheathing, ensiform, carinate, 6–8 inches long, an inch in breadth, gradually tapering to a long point: bracts lanceolate, sharply acuminate, 2 inches long, 5 lines broad; flowers about 10, large, pedicels 18 lines long; the ovary of equal length: sepals ovate, acuminate, minutely cuspidate, 8–9 lines in length; the upper one erect, scarcely at all galeate; lateral petals 2-cleft to the base, the segments linear, acute, the upper broader, not equalling the sepals; the lower very narrow, more than an inch in length: lip 3-cleft nearly to the base, exceeding an inch in length; the segments all narrow and linear, the lateral somewhat surpassing the thickish, scarcely acute central one: fleshy processes very conspicuous, linear-spatulate, 3–4 lines in length: spur over 5 inches long, exceeding the ovary and pedicel, its tip sheathed in the bracts and apparently adherent to them. — Near Guadalajara, June, 1891 (n. 3823). This striking species is related to *H. macroceratites*, Willd., and *H. setifera*, Lindl., but differs from the former in its much longer narrower leaves, larger flowers, and conspicuous fleshy appendages; from the latter, by its larger more numerous flowers, and in the shape of its petals.

Tigridia pulchella. Bulb small, oval, ½ inch in diameter, with a few fibrous roots at the base: stem slender, flexuous, 6 inches to a foot high, bearing about two narrow linear acute plicate leaves: spathe of two nearly equal lanceolate acute bracts 18 lines long, 5 lines broad: flowers solitary, about an inch in diameter: pedicel slender, an inch in length: ovary 4 lines long: outer segments of the perianth ovate-oblong; the lower part slightly broader, light colored and spotted with purple, the blunt erose somewhat recurved tips very dark purple, almost black; the inner segments shorter, more narrowed below, and with a broad yellowish minutely granular fold in the middle, the obtuse tips purple but not so dark as the outer ones: staminal column very slender, over 3 lines in length; anthers spreading, about 2 lines long: the six branches of the style with terminal capitellate stigmas. — Collected by Mr. Pringle near Patzcuaro (unnumbered and not distributed). The description of this attractive little species has been drawn from specimens cultivated and kindly communicated by Mr. Edward Gillett, of Southwick, Massachusetts.

TRADESCANTIA ANGUSTIFOLIA. A very slender grass-like species, 6 inches in height: roots of numerous delicate fibres: stems slender, glabrous, somewhat decumbent: leaves narrow, linear, very acute, 1–2 inches long, a line or less in breadth, glabrous except the ciliate margins of the sheaths: flowers small, about 3 lines in diameter, some solitary, but for the most part umbellately grouped at the ends of terminal peduncles (1–2 inches in length): the subtending bracts much shorter than the pedicels: sepals ovate, acute: petals roseate: stamens very different, the longer ones with smooth bent filaments, the broadly dilated somewhat horseshoe-shaped connective bearing the small orange-colored anther cells in a transverse position; in the shorter stamens the anthers larger, pinkish, the connective much less developed, and the cells parallel or nearly so: seeds triangular, brown, and somewhat radially rugose. — Thin soil of limestone ledges, Las Canoas, San Luis Potosi, August, 1891 (n. 3902).

XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CERTAIN PRODUCTS OF THE DRY DISTILLATION OF WOOD: METHYLFURFUROL AND METHYLPYROMUCIC ACID.*

BY HENRY B. HILL AND WALTER L. JENNINGS.

Presented November 9, 1892.

SEVERAL years ago, one of us described † the occurrence of furfurol in not inconsiderable quantity among the products of the dry distillation of wood at low and carefully regulated temperatures, as carried on at Brooklyn under the direction of Dr. E. R. Squibb. Although attempts were made at the time to separate by fractional distillation the higher boiling constituents of the crude furfurol, ordinary boiling flasks alone were employed, and the results were so far from encouraging that a more thorough investigation was for the moment relinquished. The gradual accumulation of larger quantities of these higher-boiling oils encouraged us to renew the investigation, and we soon found that fractions of constant boiling point could readily be isolated by using in the distillation the extremely effective bead columns of Hempel.‡ The most noticeable fraction which we obtained was one boiling at 184–186°. This proved to contain chiefly methylfurfurol, a preliminary account of which was published § soon after its identification. A few months later Maquenne, ‖ and Bieler and Tollens, ¶ quite independently of each other, found the same methylfurfurol among the products formed by the distillation of several species of seaweed with dilute sulphuric acid, and showed that the fucusol of Stenhouse[*] was a mixture of furfurol with this methylfurfurol. Shortly afterward the same body was obtained by the action of dilute sulphuric acid upon isodulcite by Maquenne,[†] who pointed out that this mode of formation, taking into consideration the constitution of isodulcite as established by Fischer and Tafel,[‡] proved the methyl group to be in the δ position. This conclusion of Maquenne concerning the structure of methylfurfurol was afterward confirmed in this Laboratory by a study of the product formed by the action of aqueous bromine upon methylpyromucic acid, and a brief description of this reaction was published at the time.[§] Instead of the half-aldehyde of fumaric acid

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* A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1892, by Walter L. Jennings, then candidate for the degree of Doctor of Philosophy.

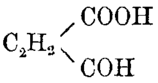
† These Proceedings, XVI. 155.

‡ Zeitschrift anal. Chem., XX. 502.

§ Berichte der deutsch. chem. Gesellsch., XXII. 607.

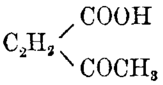
‖ Comptes Rendus, CIX. 571.

¶ Berichte der deutsch. chem. Gesellsch., XXII. 3062; Ann. Chem. u. Pharm., CCLVII. 110.



$$C_2H_2\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{COH}\end{matrix}\right.$$

which is formed under like conditions from pyromucic acid, methylpyromucic acid yields the acetacrylic acid of Wolff,[||]



$$C_2H_2\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{COCH_3}\end{matrix}\right.$$

and the formation of this ketone acid proves that the methyl group is attached to the δ carbon atom of the furfuran ring. We have also studied the action of dry bromine upon methylpyromucic acid, and have found that a somewhat unstable tetrabromide may be prepared, although the substitution products are more readily obtainable. For the preparation of the tetrabromide the temperature must be kept below 0°; if the bromine be allowed to act at ordinary temperatures a brommethylpyromucic acid is formed which melts at 150–151°, and contains the bromine in the furfuran ring, while at higher temperatures (50–60°) the bromine enters chiefly the side chain and forms ω-brommethylpyromucic acid melting at 147–148°. The formation of these two isomeric products at different temperatures recalls the analogous reactions in the aromatic series, and the analogy is completely borne out by the behavior of the two acids. We have also made a dibrommethylpyromucic acid melting at 175°, in which one bromine atom is situated in the furfuran ring, the other in the side-chain. By the action of water upon the two acids which contain halogen in the side-chain we have made the corresponding oxy-acids.

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[*] Ann. Chem. u. Pharm., LXXIV. 278.

[†] Comptes Rendus, CIX. 603.

[‡] Berichte der deutsch. chem. Gesellsch., XX. 1092; XXI. 2173.

[§] Ibid., XXIII. 452.

[||] Ibid., XX. 426; Ann. Chem. u. Pharm., CCLIV. 245.

We had intended to make a thorough study of the higher boiling fractions of the crude furfurol, and to determine as far as possible the nature of the various constituents; but the investigation of the methylfurfurol and its derivatives proved so much more attractive that we have contented ourselves with the partial examination of the fractions boiling at 200–215° and established in them the presence of guaiacol.

METHYLFURFUROL.

The material which we had at our disposal was that portion of the crude furfurol which remained behind at 175° on distilling the oil several times from ordinary retorts or boiling flasks. It had been accumulating for more than ten years, was dark in color, somewhat thick and viscous, and left on distillation a large tarry residue. We therefore distilled it from small copper retorts until signs of decomposition appeared. While the earlier investigations had shown that the temperature could be pushed to over 300° without essential decomposition, we now found that carbonization ensued at about 250°. At first we ascribed this difference in behavior to decomposition effected by long standing of the material; but we subsequently learned that changes had also been made in the mean time in the factory methods, and that it was quite possible that the greater part of our material had been subjected to the newer treatment. A special examination of the residue yielded by the distillation of nearly fifty kilograms of a fresh supply of crude furfurol showed that in this case decomposition also set in at 250°, so that no products boiling above this temperature could be obtained.

On fractioning with the aid of a Hempel column the yellow distillate which was first obtained, we soon found that it still contained considerable quantities of furfurol, and, aside from this, that a comparatively large portion distilled between 180° and 185°, and a smaller portion at 200–220°. As the distillation progressed, the intermediate fractions diminished in such a way that it became evident that but one body could be isolated between 165° and 200°, and that it boiled at a temperature not far from 185° (uncorrected). We therefore continued the distillation, taking two-degree fractions, and were able to collect a large portion which boiled with satisfactory constancy at 184–186°. As the material thus obtained showed the character of an aldehyde, a portion of it was shaken with a concentrated solution of acid sodic sulphite. The oil was almost wholly dissolved with the evolution of heat, and as the solution cooled it solidified with the separation of flat radiating prisms. These were drained thoroughly upon the pump, washed with cold alcohol, pressed, and dried. The dry crystals were then decomposed by the requisite amount of sodic carbonate in aqueous solution, and the liberated aldehyde distilled over with steam. The oil which passed over was then dried with fused calcic chloride and distilled. It showed the constant boiling point 187°, with the mercury column completely in vapor and under a pressure of 766 mm. The boiling point of a second preparation was found to be 186.5–187° under a pressure of 760 mm. An analysis of the oil showed that its formula was $C_6H_6O_2$.

0.1995 grm. substance gave 0.4788 grm. CO_2 and 0.0998 grm. H_2O.

	Calculated for $C_6H_6O_2$.	Found.
C	65.45	65.43
H	5.45	5.56

The formula of the substance, together with its strongly marked resemblance to furfurol, identified it as a methylfurfurol, and by oxidation with moist silver oxide it could readily be converted into the corresponding methylpyromucic acid.*

Freshly distilled methylfurfurol is a nearly colorless oil, with an odor closely resembling that of furfurol. On standing it grows dark-colored apparently more rapidly than furfurol, and acquires an acid reaction. The compound which it forms with acid sodic sulphite crystallizes in flat concentrically grouped prisms, which are usually rectangularly truncated. The salt dissolves in from two to three parts of water at ordinary temperatures. In the preliminary paper already referred to,† the statement was made that methylfurfurol gave the characteristic color reaction with a solution of rosaniline decolorized by sulphurous acid. We have found, however, that carefully purified methylfurfurol gives to this solution but a slight brown-red, or, if added in larger quantity, but a pale wine-red coloration, and are forced to conclude that the color formerly observed was due to a slight admixture of furfurol. It gives, however, with diazobenzol sulphonic acid when tested in the manner described by Penzoldt and Fischer [*] a color identical in shade with that given by furfurol. With hydrochloric acid and resorcine it gives an orange-red, with pyrogallol a carmine-red condensation product. Aniline acetate paper gives at first no color, or at best turns but a light yellow, but on standing a deep orange-color is developed. With phenylhydrazine a liquid hydrazone is formed, which we have not further examined. The specific gravity of methylfurfurol we have found to be somewhat higher than given by Maquenne.[†] A freshly prepared sample made with great care gave us at 18° referred to water at the same temperature the specific gravity 1.1087, or 1.1072 referred to water at 4°. As the sample was slightly colored it was distilled twice in a stream of hydrogen, but the specific gravity was altered but a few units in the fifth decimal place. The original fraction 186–187° (cor.) from which this sample was made gave a specific gravity of 1.1059. Maquenne found the specific gravity of his fraction 185–187° to be 1.107, and of the portion boiling at 187° to be 1.104. In water methylfurfurol is more sparingly soluble than furfurol, and requires about thirty times its weight of water at ordinary temperatures for complete solution.

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* See page 193.

† Berichte der deutsch. chem. Gesellsch., XXII. 607.

Since it was difficult to form even an approximate estimate of the relative amounts of furfurol and of methylfurfurol contained in the crude oil from an examination of the residues from previous distillations which we had at our disposal, we submitted to fractional distillation about 50 kilograms of the crude oil. We used a copper retort of eight litres' capacity, which was fitted with a suitable column made out of large thin-walled brass pipe and filled with glass beads. After repeated distillations we obtained about two per cent of the material taken in the fraction boiling from 182° to 186° (uncorrected), and sixty per cent in the fraction boiling from 160° to 165°. Although the absolute amounts doubtless would have been somewhat increased by further separation of the small intermediate fractions, the relative amounts could have been little altered.

Methylfurfuramide, $C_{18}H_{18}N_2O_3$.—An aqueous solution of methylfurfurol, when mixed with ammonic hydrate, gives after the lapse of some time a crystalline precipitate of methylfurfuramide. This substance crystallizes in slender radiating needles, dissolves readily in alcohol, ether, chloroform, benzol, or carbonic disulphide, but is more sparingly soluble in ligroin. The substance recrystallized from ligroin was found to melt at 86–87°, and contained the proper percentage of nitrogen.

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[*] Berichte der deutsch. chem. Gesellsch., XVI. 657.

[†] Ann. Chim. Phys., [6.], XXII. 84.

0.3510 grm. substance gave 27.8 c.c. of moist nitrogen at 22° and under a pressure of 759 mm.

	Calculated for $C_{18}H_{18}N_2O_3$.	Found.
N	9.03	8.96

GUAIACOL.

The larger fractions of the oil boiling above methylfurfurol were those which were collected between 200° and 220°, but even after long continued distillation no substances of constant boiling point could be isolated. While the oil did not appear to contain an aldehyde in sensible quantities, a large portion of it was soluble in aqueous alkalies, and we thought it advisable to take advantage of this fact in order to simplify our task. The fractions 200–215° were therefore united, shaken with a solution of sodic hydrate, and the aqueous emulsion distilled with steam as long as oil passed over. The alkaline solution was then acidified and again distilled with steam. The neutral oil when dried with calcic chloride distilled at 210–220°, and we have not yet examined it further. The oil which was soluble in the alkaline solution boiled between 200° and 205°, and the thermometer remained for a long time constant at 202°. The physical properties of this oil and the emerald-green color which ferric chloride developed in its alcoholic solution left no doubt in our minds that it was guaiacol, and we thought that it could possibly be most conveniently identified with precision by converting it into the tribromguaiacol of Tiemann and Koppe.* On adding bromine to an alcoholic solution according to their directions, however, we obtained an unsatisfactory product. The melting point, although somewhat higher than that given by Tiemann and Koppe (102°), was not sharp, and was little improved by repeated recrystallization. As the inherent disadvantages in adding bromine to an alcoholic solution were sufficiently obvious, we substituted glacial acetic acid for the alcohol, and at once obtained a definite product. From 5 grams of our oil we obtained 8.3 grams of a highly crystalline, nearly colorless bromine derivative, which melted at 111–112°, and a single recrystallization sufficed to raise the melting-point to 115–116°. Further recrystallization from alcohol or benzol failed to raise this melting-point. While our product thus melted 14° higher than the tribromguaiacol of Tiemann and Koppe, it agreed in other respects with their description, and the following analyses show that it had the same composition: —

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* Berichte der deutsch. chem. Gesellsch., XIV. 2017.

I. 0.2316 grm. substance gave 0.1974 grm. CO_2 and 0.0345 grm. H_2O.
II. 0.1603 grm. substance gave 0.2497 grm. AgBr.
III. 0.1705 grm. substance gave 0.2653 grm. AgBr.

	Calculated for $C_7H_5Br_3O_2$.	Found. I.	II.	III.
C	23.27	23.25		
H	1.39	1.65		
Br	66.48		66.30	66.24

Since we had failed to identify our substance as guaiacol through the melting point of this bromine derivative, we proceeded to prepare from it pyrocatechin. For this purpose we used, instead of the more usual hydriodic acid, hydrochloric acid, as W. H. Perkin, Jr.* had recently shown the decomposition was in this case nearly perfect if the reaction took place in sealed tube at 170–180°. On opening the tube, a gas escaped which burned with a green-bordered flame. The aqueous solution was extracted with ether, and the crystalline residue which was left upon evaporating the ether was distilled. The substance boiled at 240–242°, and the solidified distillate melted at 103–104°. When recrystallized from benzol it formed colorless lustrous scales, which appeared under the microscope to be rectangular plates, and melted sharply at 104°. The boiling point of pyrocatechin is usually given at 240–245°, and the melting point was found by Fittig and Mager † to be 104°. In aqueous solution our product also gave with ferric chloride an emerald-green coloration which turned to a violet-red on the addition of sodic carbonate. It was thus established with precision that pyrocatechin had been formed by heating with hydrochloric acid the oil under investigation, and the latter was therefore in its turn identified as guaiacol. It seems to us probable that the tribromguaiacol, which we have just described, is identical with that of Tiemann and Koppe, and that the low melting point which they observed was due to by-products introduced by their method of preparation. A more extended investigation of the matter was, however, wholly foreign to our line of work. We hope that the constituents of the crude furfurol which boil above 200° may be studied more fully in this Laboratory at some future time.

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* Journ. Chem. Soc., LVII. 589.
† Berichte der deutsch. chem. Gesellsch., VIII. 365.

METHYLPYROMUCIC ACID.

In order to prepare from methylfurfurol the corresponding methylpyromucic acid, we first attempted to follow the methods which we had already used in the manufacture of pyromucic acid from furfurol. We found, however, that alkaline hydrates, either in alcoholic or in aqueous solution,* gave us an extremely poor product in very unsatisfactory quantity. Although the experiments of Lessing in the laboratory of Limpricht † upon the oxidation of furfurol with argentic oxide, gave us little hope that we could in this way conveniently prepare large quantities of methylpyromucic acid, no better method suggested itself to us at the time, and we were forced to adopt it. To our surprise, we found that we could easily obtain in this way a weight of methylpyromucic acid which nearly equalled that of the aldehyde taken, and that we could also obtain from furfurol under the same conditions an equally satisfactory yield of pyromucic acid. From methylfurfurol we obtained as a maximum 84 per cent of the theoretical yield of methylpyromucic acid, from furfurol 82 per cent of the calculated amount of acid. As the weight of acid remaining in solution after precipitation with hydrochloric acid was in neither case taken into account, the reaction may fairly be called quantitative. The large yield which we obtained was doubtless due in part to a slight modification of the ordinary method of procedure, which we shall presently describe. Still we had no difficulty in obtaining from 10 grm. of furfurol in the usual way 8.5 grm. of argentic pyromucate, and from the acidified mother liquor by extraction with ether 2.9 grm. of pyromucic acid, so that the total yield of pyromucic acid in this case was 7.25 grm., or 62.1 per cent of the theoretical amount. All the methylpyromucic acid which we have used in our investigations we have made by the following method. 10 grm. of methylfurfurol were added to about 50 grm. of well washed argentic oxide suspended in about 800 c.c. of hot water, and the whole heated quickly to boiling. When the reaction appeared to be complete, pure sodic carbonate was added in quantity sufficient to precipitate the silver which had been carried into solution, and the feebly alkaline solution again boiled. When the fresh well marked reduction which then ensued was finished, the solution was filtered, evaporated to small volume, again filtered, and acidified with hydrochloric acid. The acid which separated as the solution cooled was nearly colorless, and as a rule a single recrystallization was sufficient to raise the melting point to the proper point. The slight color could be most conveniently removed, if necessary, by treating a solution of the calcium salt with bone-black.

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* For many years a concentrated aqueous solution of sodic hydrate has been used at this Laboratory in the preparation of pyromucic acid. Our method has been, however, essentially different from that recommended by H. Schiff (Ann. der Chem. u. Pharm., CCXXXIX. 374, CCLXI. 254), in that we have destroyed the furfuryl alcohol by hydrochloric acid instead of removing it with ether. The saving of time and of ether has more than compensated us for the somewhat diminished yield. 2 litres of furfurol are very gradually mixed with 1200 c.c. of aqueous sodic hydrate (1 : 1), taking care by constant stirring and cooling that the thick paste does not grow hot. On the following day 2 litres of concentrated hydrochloric acid are gradually added, the temperature toward the end being allowed to rise somewhat to facilitate the complete decomposition of the furfuryl alcohol. If the temperature rises too rapidly, the reaction becomes violent. The furfuryl alcohol is in any case converted into a tough leathery substance, which grows brittle on standing with the excess of hydrochloric acid. The slightly colored mother liquor is drained off, the residue crushed in an iron mortar, 4 litres of water added, and then calcic hydrate, until the solution is permanently alkaline. After standing for several days, the solution being kept slightly alkaline, the pyromucic acid is carried completely into solution. The filtrate is but slightly colored, and this slight color may be almost wholly removed by bone-black. The yield of nearly colorless pyromucic acid which may be obtained in this way amounts to from 35 to 40 per cent of the weight of furfurol taken.

† Ann. Chem. u. Pharm., CLXV. 279. Lessing obtained a weight of pyromucic acid equal to but 14 per cent of the weight of furfurol employed, or but 12 per cent of the theoretical amount.

0.2067 grm. of the acid gave 0.4321 grm. CO_2 and 0.0900 grm. H_2O.

	Calculated for $C_6H_6O_3$.	Found.
C	57.14	57.01
H	4.76	4.84

Methylpyromucic acid melts at 108–109°, and sublimes readily at low temperatures. It is readily soluble in alcohol, ether, chloroform, or hot benzol, more sparingly soluble in cold benzol, and almost insoluble in carbonic disulphide. It is extremely soluble in hot water, and on cooling it separates from concentrated solutions in short, thick six-sided prisms, or in small six-sided plates formed by the development of these prisms parallel to the basal plane. From dilute solutions it frequently separates in feathery or bladed aggregations. The solubility of the acid in cold water we determined by titration with a standard solution of baric hydrate, using phenolphthalein as an indicator.

I. 22.293 grm. of a solution saturated at 20° required for neutralization 15.3 c.c. of a solution of baric hydrate, containing 0.01864 grm. BaO_2H_2 in 1 c.c.

II. 19.665 grm. of a solution saturated at 20° required for neutralization 13.55 c.c. of the above solution of baric hydrate.

According to these determinations an aqueous solution saturated at 20° contained the following percentages of acid: —

I.	II.
1.89	1.89

Methylpyromucic acid is therefore decidedly less soluble in water at ordinary temperatures than pyromucic acid.*

For the further characterization of the acid we have prepared a number of its salts.

Baric Methylpyromucate, $Ba(C_6H_5O_3)_2$. — This salt we made by boiling an aqueous solution of the acid with baric carbonate. The salt is readily soluble in cold water, somewhat less soluble in hot water, and separates on evaporation in small colorless octahedral crystals which are anhydrous. The salt thoroughly dried by pressure suffered no material loss of weight on exposure to the air.

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* According to Houton Labillardière (Ann. Chim. Phys., [2.], IX. 368), pyromucic acid is soluble in 26 parts of water at 15°. This result is confirmed by approximate determinations made in this Laboratory as a guide in the preparation of pyromucic acid. It was found that 100 c.c. of a solution saturated at 17° contained 3.35 grm. of the acid, and that 100 c.c. of a saturated solution of sodic chloride at the same temperature dissolved 0.60 grm. of the acid. The erroneous statement made in the preliminary description of the acid (Berichte der deutsch. chem. Gesellsch., XXII. 608), that it was "somewhat more readily soluble in water" than pyromucic acid, was based upon rough quantitative results obtained in recrystallizing from water the small quantity of the acid which I then had at my disposal. — H. B. H.

I. 0.3366 grm. air-dried salt gave 0.2023 grm. $BaSO_4$.
II. 0.4261 grm. air-dried salt gave 0.2562 grm. $BaSO_4$.

	Calculated for $Ba(C_6H_5O_3)_2$.	Found. I.	Found. II.
Ba	35.40	35.34	35.34

The solubility of the salt in water at ordinary temperatures we determined in the usual way.

I. 5.8353 grm. of a solution saturated at 19°.6 gave 0.7950 grm. $BaSO_4$.
II. 5.5326 grm. of a solution saturated at 19°.6 gave 0.7526 grm. $BaSO_4$.

According to these determinations the aqueous solution saturated at 19°.6 contained the following percentages of the salt:—

I.	II
22.62	22.59

In order to determine the solubility at higher temperatures we followed essentially the method recommended by V. Meyer.*

I. 6.8590 grm. of a solution saturated at 99° gave 0.8655 grm. $BaSO_4$.
II. 5.1805 grm. of a solution saturated at 99° gave 0.6480 grm. $BaSO_4$.

The aqueous solution saturated at 99° therefore contained the following percentages of the salt: —

I.	II.
20.95	20.78

Calcic Methylpyromucate, $Ca(C_6H_5O_3)_2 \cdot 2\,H_2O$. — The calcium salt is readily soluble in cold water, and the solubility is slightly increased by heat. It crystallizes in clusters of long radiating needles which contain two molecules of water.

I. 0.3544 grm. air-dried salt gave 0.1475 grm. $CaSO_4$.
II. 0.3184 grm. air-dried salt gave 0.1333 grm. $CaSO_4$.
III. 0.8481 grm. air-dried salt lost at 110° 0.0931 grm. H_2O.
IV. 0.5421 grm. air-dried salt lost at 110° 0.0596 grm. H_2O.

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* Berichte der deutsch. chem. Gesellsch., VIII. 1002.

	Calculated for $Ca(C_6H_5O_3)_2 . 2 H_2O$.	Found. I.	II.	III.	IV.
Ca	12.28	12.24	12.31		
H_2O	11.04			10.97	10.99

I. 0.2688 grm. salt dried at 110° gave 0.1254 grm. $CaSO_4$.
II. 0.3109 grm. salt dried at 110° gave 0.1452 grm. $CaSO_4$.

	Calculated for $Ca(C_6H_5O_3)_2$.	Found I.	II.
Ca	13.79	13.72	13.74

In determining the solubility of the salt, the calcium was precipitated as oxalate and weighed as sulphate.

I. 6.8529 grm. of a solution saturated at 20°.2 gave 0.4104 grm. $CaSO_4$.

II. 7.8851 grm. of a solution saturated at 20°.2 gave 0.4688 grm. $CaSO_4$.

I.	II.
12.77	12.68

Argentic Methylpyromucate, $AgC_6H_5O_3$. — This salt may readily be made by precipitation of a soluble salt with silver nitrate, and may be recrystallized from hot water. It is sparingly soluble even in boiling water, and crystallizes from aqueous solution in fine slender needles.

I. 0.2110 grm. salt gave on ignition 0.0977 grm. Ag.
II. 0.4007 grm. salt gave on ignition 0.1855 grm. Ag.

	Calculated for $AgC_6H_5O_3$.	Found. I.	II.
Ag	46.34	46.30	46.29

Sodic Methylpyromucate, $NaC_6H_5O_3$. — The sodium salt is exceedingly soluble even in cold water. It separated from its solution in dilute alcohol after long standing in compact clusters of small anhydrous needles.

I. 0.2732 grm. air-dried salt gave 0.1325 grm. Na_2SO_4.
II. 0.4240 grm. air-dried salt gave 0.2034 grm. Na_2SO_4.

	Calculated for $NaC_6H_5O_3$.	Found. I.	II.
Na	15.53	15.60	15.53

Potassic Methylpyromucate, $KC_6H_5O_3$. — The potassium salt is also very readily soluble in cold water, and crystallizes in spherical aggregations of short prisms, which appear to be anhydrous.

0.3385 grm. air-dried salt gave 0.1790 grm. K_2SO_4.

	Calculated for $KC_6H_5O_3$.	Found.
K	23.83	23.74

Ethyl Methylpyromucate, $C_6H_5O_3C_2H_5$. — The ethyl ether of the acid we made in the ordinary way by saturating a solution in an equal weight of absolute alcohol with hydrochloric acid. The excess of hydrochloric acid was then driven off at a gentle heat, the ether precipitated with water, washed with a dilute solution of sodic carbonate, dried with calcic chloride and distilled. The whole product passed over between 212° and 215°, and by far the greater portion showed the constant boiling point 213–214° with the mercury column completely in vapor under a pressure of 766 mm. The ether showed no tendency toward crystallization when cooled with ice and salt.

I. 0.2363 grm. substance gave 0.5404 grm. CO_2 and 0.1392 grm. H_2O.

II. 0.1570 grm. substance gave 0.3585 grm. CO_2 and 0.0921 grm. H_2O.

	Calculated for $C_6H_5O_3C_2H_5$.	Found.	
		I.	II.
C	62.34	62.36	62.27
H	6.49	6.54	6.52

Methylpyromucamide, $C_6H_5O_2NH_2$. — Ethyl methylpyromucate is readily attacked by concentrated aqueous ammonia, and the reaction is completed in the cold after the lapse of two days. The clear solution then yields on evaporation the corresponding amide in long colorless prisms which melt at 131°. It is readily soluble in alcohol, dissolves freely in hot benzol or ligroin, sparingly in the cold, and may best be recrystallized from hot water, in which it is readily soluble.

I. 0.2207 grm. substance gave 22.8 c.c. of moist nitrogen at 28° and under a pressure of 762 mm.

II. 0.1839 grm. substance gave 19.1 c.c. of moist nitrogen at 26° and under a pressure of 751 mm.

	Calculated for $C_6H_5O_2NH_2$.	Found.	
		I.	II.
N	11.20	11.36	11.38

Action of Bromine and Water.

Although Maquenne* had shown that the ready formation of methylfurfurol from isodulcite led directly to the conclusion that it must contain its methyl group in the δ position, it seemed desirable to establish this point by independent facts. Since pyromucic acid could readily be oxidized by bromine in aqueous solution, and converted into well marked bodies of the maleic acid group, it seemed probable that methylpyromucic acid would also yield analogous products. It was soon found that homogeneous products could not easily be obtained by using an excess of bromine, as is the case with pyromucic acid. Although a crystalline derivative could be obtained under certain conditions, the yield was not satisfactory, and viscous products were also formed. With two molecules of bromine, however, it was easy to reach definite results. Limpricht † showed in 1873 that pyromucic acid could be converted into a body which he called the half-aldehyde of fumaric acid by the action of two molecules of bromine upon its aqueous solution, and v. Baeyer ‡ subsequently proved that fumaric acid could be formed from this by the action of argentic oxide. It was evident, if methylpyromucic acid was decomposed in an analogous fashion, that there should be formed either an homologous aldehyde acid, or a ketone acid, according to the position of the methyl group in the furfuran ring. The formation of a ketone aldehyde under these conditions did not seem possible, since Hill and Sanger § had shown that the aldehyde group in analogous reactions is invariably formed from the δ carbon of the pyromucic acid. The product formed from methylpyromucic acid under these conditions proved to be a ketone acid, and a brief description of the results of a preliminary examination which was undertaken at the time by Mr. W. S. Hendrixson ‖ and one of us was published elsewhere about two years ago. For the sake of completeness an account of these preliminary experiments will be included in the description of our own work, and we also owe to Mr. Hendrixson the analytical data which we publish. If methylpyromucic acid is suspended in about fifteen times its

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[*] Comptes Rendus, CIX. 603.

[†] Ann. der Chem. u. Pharm., CLXV. 285.

[‡] Berichte der deutsch. chem. Gesellsch., X. 1362.

[§] These Proceedings, XXI. 185.

[‖] Berichte der deutsch. chem. Gesellsch., XXIII. 452.

weight of cold water, and the vapor of bromine is slowly passed in by means of a current of air, the color of the bromine is quickly discharged, and the acid goes into solution with the escape of carbonic dioxide. When exactly two molecules of bromine have been added, the whole is allowed to stand for a short time, and the colorless solution then thoroughly extracted with ether. The ether left upon evaporation a crystalline body which was recrystallized from boiling benzol, and finally from water. An analysis showed that the formula of the substance was $C_5H_6O_3$.

0.2461 grm. substance gave 0.4734 grm. CO_2 and 0.1185 grm. H_2O.

	Calculated for $C_5H_6O_3$.	Found.
C	52.64	52.47
H	5.26	5.35

The new body was readily soluble in hot water, more sparingly soluble in cold water, and was acid in its character. It dissolved readily in alcohol, ether, or boiling chloroform, more sparingly in cold chloroform. In hot benzol it was quite readily soluble, and very sparingly soluble in cold benzol, carbonic disulphide, or ligroin. It crystallized in long slender lustrous needles, which melted at 122–123°. Recrystallization from various solvents failed to raise the melting point, but after several careful sublimations it melted at 123–124°. The formula of this acid was further controlled by an analysis of its silver salt, which was prepared by the cautious addition of ammonic hydrate to a solution of the acid containing argentic nitrate. The salt can be recrystallized from boiling water without difficulty, and forms concentrically clustered six-sided plates.

I. 0.2237 grm. salt gave 0.1901 grm. AgBr.
II. 0.2926 grm. salt gave 0.2484 grm. AgBr.

	Calculated for $AgC_5H_5O_3$	Found.	
		I.	II.
Ag	48.87	48.81	48.76

The acid which had thus been formed from methylpyromucic acid corresponded well with the description of the acetacrylic acid which Wolff * had shortly before made through the decomposition of β-bromlaevulinic acid. Its melting point, however, was given

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* Berichte der deutsch. chem. Gesellsch., XX. 426.

by Wolff as 125–125°.5, although he adds in a more recent paper* that impurities otherwise imperceptible may depress the melting point from two to three degrees. In order to compare the two acids, we have ourselves made the acetacrylic acid of Wolff from β-bromlaevulinic acid. In the preparation of the β-bromlaevulinic acid we followed with precision the directions of Wolff. The complete purification of the crude acid was in our hands attended with great loss of time and material, and, even after repeated recrystallization from carbonic disulphide, we failed to raise the melting point above 58°, while Wolff gives 59° as the melting point of the pure acid. Under these circumstances, we did not attempt to prepare pure β-bromlaevulinic acid in larger quantity, but decomposed with sodic acetate in an acetic acid solution a preparation which melted at 55–56°. The acetacrylic acid which we thus obtained was to all appearance identical with that made from methylpyromucic acid. As was to be expected, its melting point was somewhat low, 121–123°, but after several recrystallizations from benzol melted at 123–124°. Wolff† describes the silver salt of his acid as stellate needles, while the silver salt of our acid crystallized in well formed six-sided plates. We convinced ourselves that the same six-sided plates were formed by the addition of argentic nitrate to a moderately concentrated solution of both acids, and that on recrystallization these plates frequently formed dendritic aggregations. These dendritic forms only were seen if an insufficiently purified acid was used. While it is very possible that the acids which we had in our hands were in neither case absolutely pure, we cannot doubt the identity of the material from the two sources.

In order to identify still further our product with Wolff's acetacrylic acid, we dissolved it in chloroform and added at low temperature one molecule of bromine. The color of the bromine was discharged, and on evaporation a crystalline residue was obtained which melted after recrystallization from a mixture of benzol and carbonic disulphide at 107–108°. According to Wolff† the αβ-dibromlaevulinic acid melts at this point. With phenylhydrazine our product also readily gave the corresponding hydrazone, identical in every respect with the body described by Bender‡ and shortly afterward by Decker.* It crystallized in small yellow prisms, which melted at 156–157°, and dissolved in concentrated sulphuric acid with a red color. Analysis showed that it had the formula $C_{11}H_{12}N_2O_2$.

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* Ann. Chem. u. Pharm., CCLXIV. 245.

† Ibid., p. 248.

‡ Berichte der deutsch. chem. Gesellsch., XXI. 2494.

I. 0.2240 grm. substance gave 0.5299 grm. CO_2 and 0.1190 grm. H_2O.

II. 0.2173 grm. substance gave 26.6 c.c. of moist nitrogen at 23° and under a pressure of 752 mm.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found. I.	Found. II.
C	64.71	64.52	
H	5.88	5.90	
N	13.73		13.64

Bromine in aqueous solution, therefore, converts methylpyromucic acid into acetacrylic acid according to the equation

$$C_6H_6O_3 + 2\,Br_2 + 2\,H_2O = C_5H_6O_3 + CO_2 + 4\,HBr.$$

The formation of this ketone acid from methylpyromucic acid, while pyromucic acid under the same conditions yields an aldehyde acid, shows conclusively that the methyl group of the methylpyromucic acid stands in the δ place.

Action of Concentrated Sulphuric Acid.

We have thought that it might be possible to bring additional evidence as to the structure of the methylpyromucic acid through an investigation of the sulphonic acid derived from it. A study of the sulphonic acids derived from pyromucic acid had already shown that δ-sulphonic acids were always formed by the action of fuming sulphuric acid, whenever the δ hydrogen had not already been otherwise replaced; when the δ hydrogen had been thus replaced, β-sulphonic acids were formed. Moreover it was very easy to distinguish between the two isomers in that bromine in aqueous solution instantly formed sulphuric acid from the δ-sulphonic acids, while the β-sulphonic acids were oxidized to products which retained the sulpho group. Methylpyromucic acid was added with careful cooling to three times its weight of fuming sulphuric acid, the whole allowed to stand for twenty-four hours, and the diluted solution then neutralized with baric carbonate as usual. The barium salt which was obtained by evaporating the filtered solution crystallized in long needles, which were frequently collected in globular aggregations. The salt was hardly more soluble in hot than in cold water, and could best be obtained by the evaporation of its cold aqueous solution *in vacuo* over sulphuric acid. In this respect it closely resembled the baric β-sulphopyromucate. An analysis showed that the salt was baric sulphomethylpyromucate, and that it contained five molecules of water of crystallization.

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* Berichte der deutsch. chem. Gesellsch., XXI. 2937.

I. 0.4798 grm. air-dried salt gave 0.2597 grm. $BaSO_4$.
II. 0.6678 grm. air-dried salt lost at 165° 0.1383 grm. H_2O.

	Calculated for $BaC_6H_4SO_6$ $5H_2O$.	Found. I.	Found. II.
Ba	31.78	31.83	
H_2O	20.87		20.71

0.5272 grm. salt dried at 165° gave 0.3598 grm. $BaSO_4$.

	Calculated for $Ba\,C_6H_4SO_6$.	Found.
Ba	40.17	40.13

Bromine water gave in an aqueous solution of the salt no precipitate even on boiling, but after this treatment with bromine, if baric hydrate was added to alkaline reaction a white flocculent precipitate, which closely resembled baric sulphofumarate, appeared. This behavior showed conclusively that the sulpho group had not entered the furfuran ring in the δ position, and the conclusion seems warranted that it had not done so only because the methyl group already occupied that place.

Brommethylpyromucic Acids.

Bromine acts readily upon methylpyromucic acid at ordinary temperatures, and substitution is so easily effected that the isolation of an addition product is a matter of considerable difficulty. The instability of the addition product renders it unsuitable for the preparation of substituted acids, and facilitates the formation of satisfactory products by direct substitution. The nature of the products thus formed is, however, largely dependent upon the temperature at which the reaction takes place. At low temperatures the bromine enters first the furfuran ring and afterwards the methyl group, while at higher temperatures the methyl group is first attacked, although substitution apparently takes place at the same time to a certain extent in the ring. The facts which we have here observed evidently correspond precisely with those so thoroughly established in the aromatic series. Moreover, those bodies which contain the halogen in the side-chain are extremely susceptible to double decomposition, and are even decomposed by heating for a short time with water. The halogen in the main ring, on the other hand, is held quite as persistently as that in the corresponding derivatives of pyromucic acid. The study of these bodies presented at first many difficulties, the solution of which cost us so much time and labor that we have been unable to carry our researches as far as we had hoped. Since one of us must now relinquish the work, we shall present the results we have obtained, although they are in many respects incomplete. Further researches upon the subject will be made in this Laboratory. We are especially sorry that we have been unable to determine with precision the place in which the bromine enters the furfuran ring; while we have obtained by oxidation of the brommethylpyromucic acid in question an acid which is doubtless a bromacetacrylic acid, we have not yet been able to establish its structure and thus make it available in determining the constitution of the brommethylpyromucic acid from which it is formed. There can be little doubt, however, that the bromine in this case enters the β position, as it does with pyromucic acid itself as soon as the δ hydrogen atom is replaced by bromine.

β(?)-Brommethylpyromucic Acid.

When dry bromine acts at ordinary temperatures upon methylpyromucic acid, hydrobromic acid is at once evolved, and brommethylpyromucic acid is formed. The reaction is most readily controlled by the use of a solvent, and we have found glacial acetic acid most convenient for the purpose. We have found it necessary to add decidedly more than one molecule of bromine, and the best results were obtained by using three atoms. The methylpyromucic acid is dissolved in one and a half times its weight of glacial acetic acid (99.5 per cent), and the necessary amount of bromine carefully added, taking care that the temperature does not rise above 17°. After standing for some time at ordinary temperatures, the greater part of the hydrobromic acid is expelled *in vacuo* over lime, the residue poured into water, and the acid extracted with ether. The crude acid left on the distillation of the ether we have found it most advantageous to convert into the sodium salt with alcoholic sodic hydrate. The sodium salt is easily collected upon a filter, and the acid is then reprecipitated from its aqueous solution after decolorization with bone-black. The acid may be further purified by several repetitions of the same process.

I. 0.2279 grm. substance gave 0.2935 grm. CO_2 and 0.0526 grm. H_2O.

II. 0.1147 grm. substance gave 0.1055 grm. AgBr.

	Calculated for $C_6H_5BrO_2$.	Found. I.	Found. II.
C	35.12	35.13	
H	2.44	2.56	
Br	39.02		39.15

Brommethylpyromucic acid crystallizes in colorless branching needles, which melt at 150–151°. It is readily soluble in alcohol, ether, or chloroform, somewhat sparingly soluble in cold, more readily in hot benzol. In carbonic disulphide or ligroin it dissolves but sparingly even on boiling. It is somewhat sparingly soluble in hot water, and is deposited in clusters of branching needles as the solution cools. The solubility of the acid in water at ordinary temperatures we determined in the usual way. We neutralized with baric carbonate the solution of the acid, and determined as sulphate the barium which had been dissolved.

I. 17.598 grm. of a solution saturated at 21°.4 gave 0.0271 grm. $BaSO_2$.

II. 16.031 grm. of a solution saturated at 21°.4 gave 0.0264 grm. $BaSO_4$.

The aqueous solution saturated at 21°.4 therefore contained the following percentages of the acid: —

I.	II.
0.27	0.29

For the further characterization of the acid we also prepared certain of its salts.

Baric Brommethylpyromucate, $Ba(C_6H_4BrO_3)_2 \cdot 4\,H_2O$. — This salt may readily be made from a solution of the ammonium salt by precipitation. It is sparingly soluble in cold water, more readily soluble in hot water, and crystallizes from the hot aqueous solution on cooling in dendritic needles, which contain four molecules of water. The salt is permanent in the air, but effloresces rapidly over sulphuric acid.

I. 0.4478 grm. air-dried salt gave 0.1690 grm. $BaSO_4$.
II. 0.8747 grm. air-dried salt lost at 110° 0.1030 grm. H_2O.

	Calculated for	Found.	
	$Ba(C_6H_4BrO_3)_2 . 4\,H_2O$.	I.	II.
Ba	22.20	22.19	
H_2O	11.67		11.78

0.3664 grm. salt dried at 110° gave 0.1558 grm. $BaSO_4$.

	Calculated for $Ba(C_6H_4BrO_3)_2$.	Found.
Ba	25.14	25.00

The solubility of the salt in cold water was determined in the usual way.

I. 19.211 grm. of a solution saturated at 20°.2 gave 0.0518 grm. $BaSO_4$.
II. 19.984 grm. of a solution saturated at 20°.2 gave 0.0466 grm. $BaSO_4$.

The aqueous solution saturated at 20°.2 therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.63	0.55

Calcic Brommethylpyromucate, $Ca(C_6H_4BrO_3)_2 . 3\,H_2O$.—The calcium salt we prepared by precipitating with calcic chloride an ammoniacal solution of the acid. It crystallized from hot water in clusters of short needles which contained three molecules of water. The salt was permanent in the air, and lost but little in weight over sulphuric acid.

I. 0.2508 grm. air-dried salt gave 0.0680 grm. $CaSO_4$.
II. 0 5443 grm. air-dried salt lost at 110° 0.0584 grm. H_2O.

	Calculated for	Found.	
	$Ca(C_5H_4BrO_3)_2 . 3\,H_2O$.	I.	II.
Ca	7.97	7.98	
H_2O	10.76		10.73

0.2724 grm. salt dried at 110° gave 0.0584 grm. $CaSO_4$.

	Calculated for $Ca(C_6H_4BrO_3)_2$.	Found.
Ca	8.93	8.86

In determining the solubility of the salt the calcium was precipitated as oxalate, and converted into sulphate before weighing.

I. 15.373 grm. of a solution saturated at 20° gave 0.0189 grm. $CaSO_4$.

II. 13.879 grm. of a solution saturated at 20° gave 0.0170 grm. $CaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.41	0.40

Argentic Brommethylpyromucate, $AgC_6H_4BrO_3$. — The silver salt crystallizes from hot water in spherical aggregations of dendritic needles.

0.0956 grm. salt gave 0.0574 grm. AgBr.

	Calculated for $AgC_6H_4BrO_3$.	Found.
Ag	34.61	34.48

Potassic Brommethylpyromucate, $KC_6H_4BrO_3$. — This salt is very readily soluble even in cold water, and crystallizes on slow evaporation of its aqueous solution in small anhydrous needles.

0.2789 grm. salt gave 0.0993 grm. K_2SO_4.

	Calculated for $KC_6H_4BrO_3$.	Found.
K	16.08	15.99

Action of Bromine and Water.

The whole behavior of the brommethylpyromucic acid showed conclusively that its bromine atom was situated in the furfuran ring. Although the bromacetacrylic acids had not yet been made, one of which would doubtless be formed by the oxidation of this brommethylpyromucic acid, and we therefore could not hope to determine whether the bromine was in the β or in the γ position, we nevertheless thought it best to investigate the products of oxidation. Brommethylpyromucic acid was suspended in thirty times its weight of water, and somewhat more than two molecules of bromine then slowly passed in by means of a current of air. The acid was readily carried into solution, and at the same time a small amount of an insoluble substance was formed. The filtered solution was extracted with ether, and the ethereal extract dried with calcic chloride. The viscous residue which was left on the distillation of the ether gradually solidified on standing over sulphuric acid *in vacuo*. This body proved to be an acid, containing bromine, readily soluble in water, but crystallizing from benzol by evaporation in rosettes. The melting point of the recrystallized acid was found to be 61°. An analysis showed that the percentage of bromine contained in this acid agreed with that required by a bromacetacrylic acid.

0.1630 grm. substance gave 0.1594 grm. AgBr.

	Calculated for $C_5H_5BrO_3$.	Found.
Br	41.45	41.62

The oxidation had therefore taken precisely the same direction as that followed by the analogous decomposition of methylpyromucic acid, and through this product of oxidation it will doubtless be possible at some future time to fix the constitution of the brommethylpyromucic acid. A product apparently identical with this we have also obtained by the action of dilute nitric acid.

The insoluble product formed at the same time with the bromacetacrylic acid we unfortunately have not been able to study further. It is not acid in its character, contains a large amount of bromine, and crystallizes from benzol in long colorless prisms, which melt at 90–91°.

ω-BROMMETHYLPYROMUCIC ACID.

Although bromine in acting upon methylpyromucic acid at ordinary temperatures enters at once the furfuran ring, at the temperature of boiling carbonic disulphide or chloroform it attacks chiefly the methyl group, and a bromine derivative is formed in considerable quantity which differs wholly in its properties from the acid just described. The reaction is not perfectly simple, for we have found that we could obtain the best yield of the new product by using twice the theoretical quantity of bromine. We have dissolved the methylpyromucic acid in six times its weight of chloroform and slowly added to the boiling solution two molecules of bromine diluted with its own weight of chloroform. The evolution of hydrobromic acid at once begins, and frequently before the bromine is all added a heavy crystalline body separates from the hot solution. When the reaction is over, the chloroform is well cooled, the crystalline product, which amounts to about sixty per cent of the weight of methylpyromucic acid taken, filtered off, and washed with cold chloroform. It may then be recrystallized from boiling chloroform or benzol.

I. 0.2152 grm. substance gave 0.2758 grm. CO_2 and 0.0490 grm. H_2O.

II. 0.1176 grm. substance gave 0.1079 grm. AgBr.

	Calculated for $C_6H_5BrO_3$.	Found.	
		I.	II.
C	35.12	34.95	
H	2.44	2.53	
Br	39.02		39.04

The ω-brommethylpyromucic acid crystallizes in small clustered oblique plates which melt at 147–148°. It is readily soluble in alcohol, ether, glacial acetic acid, or acetone, somewhat sparingly soluble in boiling benzol or chloroform, from which solvents it crystallizes well on cooling. In boiling toluol it is freely soluble, sparingly soluble in the cold, and almost insoluble in carbonic disulphide. It is but slowly acted on by cold water, but on warming it is readily dissolved with decomposition. The solution contains hydrobromic acid in abundance, and upon evaporation a crystalline acid is obtained, which is free from bromine. This behavior, which is in such striking contrast with the extreme stability of the derivatives of pyromucic acid that contain halogen, sufficiently establishes the position of the bromine in the side-chain. It also effectually prevented the preparation of its salts by the ordinary methods.

Decomposition by Water.

The product formed by the action of water upon ω-brommethylpyromucic acid we have studied a little more in detail. After heating an aqueous solution for some time at 100° it was evaporated over lime *in vacuo*. The hard black crystalline residue was dissolved in hot water, filtered from the separated carbon, and again evaporated. The brownish vitreous crystalline mass thus obtained melted with decomposition at 158–162°, and by recrystallization from a mixture of toluol and absolute alcohol the melting point could be raised to 162–163°, although the body still melted with decomposition. A combustion showed that the substance was ω-oxymethylpyromucic acid.

0.2623 grm. substance gave 0.4870 grm. CO_2 and 0.1052 grm. H_2O.

	Calculated for $C_6H_6O_4$.	Found.
C	50.70	50.63
H	4.23	4.46

ω-Oxymethylpyromucic acid is readily soluble in water, alcohol, or glacial acetic acid. In ether it is but slightly soluble, and in benzol, toluol, chloroform, or carbonic disulphide it is almost wholly insoluble. The barium salt of the acid is readily soluble in water, and is left as a varnish as its aqueous solution evaporates. From concentrated solutions it is thrown down as a flocculent precipitate on the addition of alcohol. We have not yet examined it further, and we have as yet found no other salts of a more inviting character.

The ease with which the ω-brommethylpyromucic acid entered into reaction with water naturally suggested the study of its behavior with other reagents. Unfortunately, we were unable to pursue our investigations in this direction, but further researches will be made in this Laboratory.

In the preparation of the ω-brommethylpyromucic acid small quantities of the isomeric acid were also apparently formed. From the chloroform mother liquors we obtained, after treatment with water and baric carbonate, a small amount of a crystalline acid which melted at 149–151°, and in other respects resembled the brommethylpyromucic acid first described.

ωβ(?)-DIBROMMETHYLPYROMUCIC ACID.

If the brommethylpyromucic acid melting at 150–151° is treated with bromine in boiling chloroform, a second atom of bromine enters the side-chain and a dibrommethylpyromucic acid is formed. The acid which separates on cooling or after partial evaporation of the solvent is washed with cold chloroform, and recrystallized from boiling toluol. This acid may perhaps more economically be made by the direct action of bromine at ordinary temperatures. Methylpyromucic acid is exposed over night to the vapor of three times its weight of bromine. The semiliquid product is well washed with carbonic disulphide, next with chloroform, and the dry crystalline residue recrystallized from boiling toluol. Our analyses are not altogether satisfactory, but they leave no doubt as to the nature of the body.

I. 0.2877 grm. substance gave 0.2735 grm. CO_2 and 0.0418 grm. H_2O.

II. 0.2086 grm. substance gave 0.2748 grm. AgBr.

	Calculated for $C_6H_4Br_2O_3$.	Found. I.	Found. II.
C	25.35	25.92	
H	1.41	1.61	
Br	56.33		56.07

This dibrommethylpyromucic acid crystallizes in small oblique tabular crystals, which melt at 175° with decomposition. It is readily soluble in alcohol, ether, or glacial acetic acid, is but sparingly soluble in boiling benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. In boiling toluol it is quite readily soluble.

Action of Water.

On warming with water the acid is decomposed, hydrobromic acid is formed, and the solution then contains an oxybrommethylpyromucic acid. We prepared this acid first by treating with water the product formed by the vapors of bromine upon methylpyromucic acid, and separating it from the brommethylpyromucic acid melting at 151° which accompanied it by washing the mixed acids with benzol. The acid thus prepared from the crude material was absolutely identical with that afterwards made from the pure dibrommethylpyromucic acid. For analysis the substance was crystallized from a mixture of benzol and alcohol.

I. 0.1950 grm. substance gave 0.2333 grm. CO_2 and 0.0420 grm. H_2O.

II. 0.1695 grm. substance gave 0.1445 grm. AgBr.

	Calculated for $C_6H_5BrO_4$.	Found. I.	II.
C	32.58	32.63	
H	2.26	2.39	
Br	36.20		36.28

The ω-oxy-β(?)-brommethylpyromucic acid is readily soluble in alcohol and ether, very sparingly soluble in boiling carbonic disulphide, somewhat more readily soluble in boiling chloroform, from which it separates on cooling in obliquely terminated prisms. It is sparingly soluble in hot benzol, and almost insoluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and separates from dilute aqueous solutions in large obliquely terminated prisms, which contain one molecule of water. The crystals effloresce slowly over sulphuric acid, or even in the air after months of exposure, but we were unable to dehydrate them by heat without bringing about slight decomposition.

I. 0.4413 grm. of acid crystallized from water lost over sulphuric acid 0.0328 grm. H_2O.

II. 0.2117 grm. of acid dried in desiccator over night gave 0.1681 grm. AgBr.

	Calculated for $C_6H_5BrO_4 . H_2O$.	Found. I.	Found. II.
H_2O	7.53	7.43	
Br	33.47		33.80

The anhydrous acid melts at 153–154°, and on cooling forms a viscous gummy mass. Sodium amalgam reduces the acid without difficulty, and yields the ω-oxymethylpyromucic acid already described. The barium salt of the acid is readily soluble in water, and crystallizes in clustered short needles, but we have made no further study of its salts.

METHYLPYROMUCIC TETRABROMIDE.

We have already spoken of the instability of the addition product which methylpyromucic acid forms with bromine. We succeeded in isolating it by adding two molecules of bromine diluted with a little chloroform to a solution of methylpyromucic acid in five times its weight of chloroform well cooled with ice and salt. The bromine was slowly added with constant shaking, and at this low temperature but little hydrobromic acid was noticed. The addition product soon began to separate in flat colorless needles, which were frequently twinned at right angles. After the bromine had all been added, the whole was allowed to stand for a short time, and the product then quickly filtered upon the pump and washed with cold chloroform. It was then pressed with filter paper and dried in desiccator. As we found it impossible to recrystallize the substance without serious decomposition, we analyzed it without further purification. On exposure to moist air it rapidly liquefied, and even over sulphuric acid it soon evolved hydrobromic acid in abundance. Analyses IV. and V., made with material which had stood for two and four days respectively in desiccator, show how rapidly the decomposition progresses.

I. 0.2695 grm. substance gave 0.1668 grm. CO_2 and 0.0383 grm. H_2O.
II. 0.3509 grm. substance gave 0.2182 grm. CO_2 and 0.0467 grm. H_2O.
III. 0.2011 grm. substance freshly made gave 0.3393 grm. AgBr.
IV. 0.1564 grm. of same substance after two days gave 0.2601 grm. AgBr.
V. 0.1520 grm. of same substance after four days gave 0.2513 grm. AgBr.

	Calculated for $C_6H_6Br_4O_3$.	Found. I.	II.	III.	IV.	V.
C	16.14	16.88	16.96			
H	1.35	1.58	1.48			
Br	71.74			71.81	70.79	70.37

Methylpyromucic tetrabromide is very sparingly soluble in carbonic disulphide or ligroin, somewhat less sparingly soluble in chloroform or benzol. In hot chloroform or benzol it dissolves more freely, but decomposition evidently ensues, for little unaltered substance crystallizes on cooling. The substance melts at about 95° with decomposition, but the melting point varies with the rapidity with which it is heated. Although the addition product is so unstable we have been able to find but few definite products resulting from its decomposition. Alcoholic sodic hydrate apparently destroys it completely. Sodic acetate in glacial acetic acid gives the brommethylpyromucic acid melting at 150–151°, and the same acid also appears to be formed in the spontaneous decomposition of the body when exposed to the air.

Further investigations in this direction will be made in this Laboratory.

XIV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CERTAIN DERIVATIVES OF PYROMUCAMIDE.

By Charles E. Saunders.

Presented by Henry B. Hill, November 9, 1892.

This investigation was undertaken at the suggestion of Professor H. B. Hill, in the hope of obtaining from pyromucamide or its derivatives, through Hofmann's * reaction, an amine having the nitrogen atom directly united to a carbon atom of the furfuran ring, no such amine being at present known. Since preliminary experiments with pyromucamide had shown that the reaction was complicated by products formed through the action of the bromine upon the furfuran group, βδ-dibrompyromucamide was chosen as better adapted to the purpose, since the corresponding acid is unaffected by bromine. In this case, however, the product proved to be the nitrile of the acid, instead of the amine, with one less carbon atom. The behavior of pyromucamide with dry bromine was next studied, and a stable tetrabromide isolated, and at the same time the action of bromine in aqueous solution upon pyromucamide was examined in order to find an explanation of certain striking color reactions which had previously been observed in this Laboratory.

The Action of Bromine and Potassium Hydroxide on βδ-Dibrompyromucamide.

Bromine alone has no marked action on βδ-dibrompyromucamide, the amide dissolving quietly in the bromine. On evaporating, the amide can be recovered unchanged, though the removal of the last portions of bromine at ordinary temperatures occupies considerable time, indicating perhaps the production of an unstable tetrabromide. Nevertheless, all attempts to prove more definitely the formation of such a product failed. When the amide was dissolved in bromine and the solution treated with aqueous potassium hydroxide, a small yield of a substance insoluble in water was obtained. This was filtered off, washed with water, and distilled with steam. The best yield was obtained as follows. One part of the amide was dissolved in 1.8 parts of bromine (about six atoms of bromine to one molecule of amide) in a large beaker. Over this solution was poured a considerable quantity of a cold five per cent solution of sodium or potassium hydroxide. The contents of the beaker were kept cold, and allowed to stand, the alkaline reaction being maintained by the occasional addition of a small portion of 20 per cent sodium hydroxide solution. The insoluble product gradually rose to the surface, as the bromine disappeared, and was skimmed off. It was washed with dilute acid, and then distilled with steam. The yield was nearly 13 per cent of the weight of amide taken. For further purification the substance was crystallized from a very small quantity of alcohol, solution being brought about at 90° to 100° under pressure.

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* Berichte der deutsch. chem. Gesellsch., XIV. 2725; XV. 407, 752, 762; XVII. 1406, 1923; XVIII. 2734.

The substance gave the following results on analysis: —

I. 0.4259 grm. substance gave 0.3745 grm. CO_2 and 0.0160 grm. H_2O.
II. 0.2044 grm. substance gave 0.3082 grm. Ag.Br.
III. 0.2056 grm. substance gave 10.3 c. c. of moist nitrogen at 15°.3 and 757.5 mm. pressure.

	Calculated for C_5HBr_2NO.	Found. I.	II.	III.
C	23.90	23.98		
H	0.40	0.42		
Br	63.75		64.17	
N	5.58			5.84

The analysis shows that the substance is not the expected amine, but is $\beta\delta$-dibromfurfuronitrile. This conclusion was confirmed by the reactions of the substance, and by its preparation through the dehydration of the amide, using phosphorus pentachloride as the dehydrating agent. The amide was mixed with the calculated quantity of phosphorus pentachloride, and the mixture heated in a distilling flask to about 200°, until hydrochloric acid ceased to be given off. The contents of the flask were then distilled with steam. The yield of dibromfurfuronitrile was 56 per cent of the calculated amount. The substance as thus obtained was found to be identical in composition and physical properties with that formed by the action of bromine and dilute potassium hydroxide on the dibromamide. A combustion of this product gave the following results: —

0.4272 grm. substance gave 0.3793 grm. CO_2 and 0.0217 grm. H_2O.

	Calculated for C_5HBr_2NO.	Found.
C	23.90	24.21
H	0.40	0.56

Properties of βδ-Dibromfurfuronitrile. — It is a colorless solid, possessing a characteristic and rather pleasant odor. It is volatile with steam, scarcely at all soluble in water, readily soluble in ether and in hot alcohol (especially at 100° under pressure). Its melting point is 88° (uncor.), and its boiling point 225° (uncor.). It can be sublimed. It crystallizes from superheated alcohol in leaflets or plates. On standing for several days in a warm room with concentrated hydrochloric acid, it is converted into βδ-dibrompyromucamide. When it is heated for about an hour in a sealed tube at 100° with concentrated hydrochloric acid, a considerable amount of βδ-dibrompyromucic acid is formed. Prolonged heating causes blackening.

These two reactions were tried with the nitrile prepared in both ways. In alcoholic solution sodium amalgam formed no reduction product. The nitrile was dissolved in dilute alcohol, and treated with two per cent sodium amalgam, a current of carbon dioxide being passed through until the action was over. The distillate obtained from this was not alkaline, and gave practically no residue when acidified and evaporated. The residue in the flask gave, on evaporation, needles of βδ-dibrompyromucamide.

When the solution of dibromamide in bromine was treated with dilute cold potassium or sodium hydroxide, the only product found, beside the nitrile, was monobrommaleic acid. This was identified by its melting point and other physical properties, as well as those of its barium salt.

The dehydration of the dibromamide, — under the conditions of the experiments related, — with formation of the nitrile, is particularly interesting, because Hofmann* found that, in preparing amines from amides by the method introduced by him, nitriles were sometimes produced, chiefly when working with the amides of the higher fatty acids; but the nitriles thus formed always contained one carbon atom less than the amide with which he started, and he considers the amine to be an intermediate product in these cases. In the present instance, however, since the nitrile contains the same number of carbon atoms as the amide, this interpretation of the reaction cannot be applied. The author has no explanation to offer. It is worthy of note that the same reaction takes place, whether the alkali used is potassium, sodium, or barium hydroxide.

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* Berichte der deutsch. chem. Gesellsch., XVII. 1406, 1920.

The Action of Bromine on Pyromucamide.

The tetrabromide of pyromucamide is obtained by dropping small portions of powdered pyromucamide into bromine kept cooled below zero. One should use 3.6 parts of bromine to one part of pyromucamide; that is, about five atoms of bromine to one molecule of pyromucamide. The liquid becomes thick and should be well stirred. After the pyromucamide has all been added, the excess of bromine is allowed to evaporate, and cold alcohol poured over the well cooled residue. On standing, a pale yellow, finely divided solid is separated from the dark mass. After the latter has been completely broken up, the product is filtered off and washed with ether. The yield is between 50 and 60 per cent of the calculated amount. For further purification the substance is dissolved in ethyl acetate or acetone, and the greater part of the solvent distilled off. It is then filtered, and washed again with ether. The substance is thus obtained in minute, colorless, glistening crystals. An analysis gave the following results: —

I. 0.3417 grm. substance gave 0.1751 grm. CO_2 and 0.0410 grm. H_2O.
II. 0.1110 grm. substance gave 0.1950 grm. AgBr.
III. 0.4586 grm. substance gave 13.6 c.c. of moist nitrogen at 23°.5 and 765 mm. pressure.

	Calculated for $C_5H_5NBr_4O_2$.	Found.		
		I.	II.	III.
C	13.92	13.98		
H	1.16	1.33		
Br	74.25		74.76	
N	.25			3.36

The substance is therefore the tetrabromide of pyromucamide.

Properties of Pyromucamide Tetrabromide. — It is a crystalline solid without color or odor. Its melting point is about 121°, as determined in the ordinary way, but it varies with the rapidity of the heating. By long heating the substance will melt, always with evident decomposition, even below 100°. It is insoluble in water, almost insoluble in ether, chloroform, glacial acetic acid, or alcohol, somewhat more readily soluble in ethyl acetate and acetone. It is decomposed by boiling with water, alcohol, or glacial acetic acid. When it was dissolved in alcohol and treated with zinc dust in the cold, the bromine was abstracted and pyromucamide formed. On boiling with water it is decomposed; hydrobromic acid is formed, but no definite organic compound could be isolated. In order to study the products formed by the action of alkalies, the tetrabromide was added gradually, in small portions, to *cold* concentrated alcoholic sodium hydroxide. After standing in the cold for about an hour, the mixture was allowed to remain for several days in a warm room, the alcohol being renewed when necessary. Ammonia was slowly evolved. The alcohol was then evaporated off, and the solid residue treated with water. Only a very small portion of insoluble matter was left. This was filtered off. On acidifying the filtrate, an acid was precipitated which was purified by converting it into the barium salt, and separating the latter by fractional crystallization into three portions. The acid was then liberated from each portion separately. It appeared to be $\beta\gamma$-dibrompyromucic acid, since each fraction melted at about 192°, the purest at 191°.5. To remove all doubt, this portion was dissolved in absolute alcohol, and converted into the ethyl ester by the action of dry hydrochloric acid. The observed melting point of the ester, 67°.5, completed the proof as to the nature of the acid, since the $\beta\gamma$-dibrompyromucic acid melts at 191–192°, and its ethyl ester at 67–68°.* $\beta\delta$-dibrompyromucic acid does not seem to be formed at all in this decomposition of pyromucamide tetrabromide. Even microscopic examination failed to prove its presence, though the crystals are quite characteristic. This is interesting in consideration of the fact observed by Hill and Sanger,* that the tetrabromide of pyromucic acid yields, under similar circumstances, a mixture of the two isomeric dibrompyromucic acids ($\beta\gamma$ and $\beta\delta$).

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* These Proceedings, XXI. 155 *et seq.*

The Action of Bromine Water on Pyromucamide.

Some remarkable color reactions observed by Professor Hill, when studying the action of bromine and potassium hydroxide on pyromucamide, led to the suggestion that interesting results might be obtained in that direction by further work. The author therefore gave a short time to the study of the nature of these color reactions, as well as those produced when bromine water is used in place of pure bromine, and when other basic substances are used in place of potassium hydroxide.

Pyromucamide treated with bromine water dissolves readily, producing a solution almost or quite colorless. This was treated in various ways in order to isolate, if possible, some definite substance from it, but amorphous dark products were always obtained. If to the fresh solution there is added almost any strongly basic inorganic substance, a dark blue (or sometimes purple) color is soon produced, the rapidity of its production depending apparently on the strength of the base. The color usually changes to purple in a short time, and afterwards undergoes other alterations, generally passing to red, and finally, if the amount of pyromucamide used is small, fading to pale yellow. When the base employed is barium hydroxide, a dark blue amorphous precipitate is produced. An investigation was made as to the quantity of bromine required to produce the maximum intensity of color from a given amount of pyromucamide. Measured quantities of dilute solutions of pyromucamide and bromine were mixed, shaken, and allowed to stand a few moments. Then an excess of sodium hydroxide was added, and the colors produced were compared. It was found that two atoms of bromine to each molecule of pyromucamide gave the deepest color on subsequent treatment with alkali. Either a deficiency or an excess of bromine is unfavorable to the color production. The dark blue compound was too unstable for isolation.

The production of this color may serve as a very delicate test for pyromucamide. When one milligram of the amide is dissolved in a drop of dilute bromine water, and the solution made alkaline, the blue (or purple) color produced is quite distinct.

Chlorine water can be used instead of bromine water, but the color was not obtained when iodine or nitric acid was employed. Substituted pyromucamides, so far as investigated, do not give the color reaction: δ-methylpyromucamide, βδ-dibrompyromucamide, and βγ-dichlorpyromucamide were tried.

If, instead of sodium hydroxide, an aqueous solution of aniline is added to the solution of pyromucamide in bromine water, a *reddish precipitate* is produced. This substance is not stable. It melts at about 78°, and appears to undergo decomposition when treated with alcohol even in the cold.

By substituting a saturated aqueous solution of phenyl hydrazine for aniline, a brilliant red precipitate was obtained. The most convenient method for preparing this substance is as follows. Dissolve a weighed amount of pyromucamide in as small a quantity of water as convenient; add to this bromine, a few drops at a time, shaking the flask and keeping it cool, until for each molecule of pyromucamide two atoms of bromine have been added. The bromine will be dissolved, and the solution will be almost colorless. Filter if necessary, and add a large excess of a saturated solution of phenyl hydrazine in water. Allow the mixture to stand for some time, filter off the red precipitate formed, wash with water, then with two or three small portions of alcohol, and lastly with ether. Dry over sulphuric acid or in a steam-drying oven. The yield is about 1.6 times the weight of the amide taken. The substance as thus obtained is bright red in color. It has no definite melting point, but darkens in color between 150° and 160°. It is dissolved, and probably decomposed, by aqueous or alcoholic potassium hydroxide, with a marked increase in the intensity of the red color. It is very slightly soluble in chloroform, ether, and carbon disulphide, somewhat more readily in alcohol and acetone. Boiling with alcohol and other solvents decomposes it, but it can be obtained in small scale-like crystals by making a saturated solution at 50° in alcohol or acetone, and allowing it to cool and evaporate spontaneously. The crystals are darker in color than the amorphous material, and are quite brilliant. Qualitative tests showed the absence of bromine. Analyses of the substance, both in the crystalline and the amorphous state, were made with identical results.

The material used in analyses I. and II. was crystallized from acetone, washed with ether and dried at 100°, while in analyses III. and IV. an amorphous preparation was used which had been washed successively with water, alcohol, and ether, and dried over sulphuric acid.

I. 0.3001 grm. substance gave 0.6684 grm. CO_2 and 0.1423 grm. H_2O.

II. 0.1005 grm. substance gave 17.2 c.c. of moist nitrogen at 23°.5, and 754 mm. pressure.

III. 0.1740 grm. substance gave 0.3879 grm. CO_2 and 0.0857 grm. H_2O.

IV. 0.2196 grm. substance gave 37.9 c.c. moist nitrogen at 21°.5, and 741 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_2$.	Found.			
		Crystalline.		Amorphous.	
		I.	II.	III.	IV.
C	60.83	60.74		60.80	
H	5.07	5.27		5.47	
N	19.35		19.08		19.10

The formula of the substance $C_{11}H_{11}N_3O_2$ shows that it contains the elements of one molecule of phenyl hydrazine, and one of pyromucamide, less two atoms of hydrogen. Lack of time prevented a more extended study of this body, but the investigation will be continued at some future time in this Laboratory.

XV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXVIII. — ON THE LEAST NUMBER OF VIBRATIONS NECESSARY TO DETERMINE PITCH.

By Charles R. Cross and Margaret E. Maltby.

Presented May 24, 1892.

The present paper is an extension of one by the same authors read at the meeting of this Academy held on June 10, 1891, but not hitherto published. In the investigation described in it a method was employed which was originally proposed by one of the writers a number of years since in a paper read at the Philadelphia Meeting of the American Association for the Advancement of Science, and published in abstract in the Proceedings for 1884, Vol. XXXIII. p. 114.

In that paper attention was called to a defect in the method employed by Savart and Kohlrausch, from which they concluded that at least two complete vibrations are necessary to characterize pitch. This defect is a consequence of the character of the vibrations impressed upon the air by the blows produced by the teeth of the wheel of Savart or the comb of Kohlrausch.

The statement of this difficulty in the paper referred to is as follows: —

"A cardinal defect in these methods of investigating the point in question is that the sound produced by a toothed wheel is very impure; first, because the noise of each separate impulse is mingled with the note produced by the coalescence of the separate impulses; and second, because the proper note, determined by the number of impulses, is itself far from simple in its character. To obtain results that are fully satisfactory the vibrations utilized should be pendular (sinusoidal) in their character. I see no reason in the nature of things why, if a single such simple vibration could be caused to fall upon the ear, it should not produce the sensation of a definite pitch. Rather, under the known action of the separate vibrating parts of the ear, we might suppose that even a small portion of a simple sound-wave, if it produced any recognizable sensation, would give a sound of a pitch corresponding to the length of the complete sound-wave, of which a part had impressed the ear."

The method devised in 1884 to remedy the defect consisted of a telephonic circuit containing two magneto-telephones, connected in the usual manner for the transmission of sound, and a circuit-making wheel. The latter was a wheel of vulcanite, furnished with a single narrow conducting strip of brass extending over a small arc of its circumference. Against the edge of the disk pressed a spring whose end was faced with platinum. If such a wheel is revolved at a uniform speed, it is clear that once in each revolution the circuit between the two telephones is closed for a brief period, whose duration can readily be determined when the speed of the wheel and the angular extent of the conducting sector are known. If now the sound of a tuning-fork giving simple harmonic vibrations actuates the transmitting telephone, the electrical undulation produced will be a sinusoidal one, and the air-waves produced at the receiver will be substantially similar in character, and continuous, provided the contact-making spring rests upon the metal sector of the wheel so as to complete the circuit. But if the wheel is revolved the electrical current is broken, except during a brief interval of time when the spring is in contact with the metallic sector; at which period, however, a current of brief duration is sent through the line and a correspondingly brief sound is produced at the receiver. Except in so far as self-induction and like phenomena act to prevent this, these brief electrical currents are still sinusoidal in character; and hence should give rise at the receiving telephone to waves or portions of a wave of sound which are sinusoidal in form, and should be perceived by the ear as a simple tone. In so far as the motion of the diaphragm of the receiver deviates from a simple harmonic one, either from disturbing electrical effects due to self-induction, or from the acoustic effect of the sudden pull and relaxation which occur when the circuit is made and broken by the contact-making spring, disturbing sounds will of course be added to the simple tone, which would otherwise be the only one produced. But unless the disturbing causes are excessive, the pitch of the simple tone corresponding to that given by the tuning-fork actuating the transmitter will predominate. And as a matter of fact these disturbances are slight, as is shown by the fact that there is no difficulty in transmitting speech through a circuit with a magneto-transmitter at one end and a magneto-receiver at the other, when a rapidly revolving circuit-breaking wheel is interposed to interrupt the current as many as thirty times per second and upwards. At high rates of circuit-breaking the high-pitched note, due to the interruptions, is simply added to the vocal sounds transmitted.

In practice, however, a slight modification of the apparatus described was found to be necessary. As had been surmised when the apparatus was originally devised, clicks and scratches were heard in the receiving telephone when the current was rapidly made and broken by the revolving wheel. These often masked the proper sound of the fork. They seemed to be due to microphonic action at the contact of the spring and brass segment; and although we found that this could often be avoided by careful smoothing of the contact surfaces and proper adjustment of pressure, yet it was difficult to keep the apparatus in good adjustment. For this reason, we substituted for the vulcanite wheel a brass wheel having a single insulating segment of vulcanite. The receiving telephone, whose resistance was 115 ohms, was placed in derivation with the brass wheel, so that during the greater part of the time the receiving telephone was short-circuited and no sensible current passed through it, as the wheel had very slight resistance. But whenever the spring rested on the vulcanite segment the circuit through the wheel was broken; and hence a current passed through the receiving telephone and produced a sound. This arrangement obviated the difficulty just referred to, although care had to be taken to keep the contacts in good condition, as otherwise more or less of a scratching sound was introduced. In order to reduce the resistance of the short circuit through the wheel to a minimum, the current was caused to enter the wheel in the following manner. A disk made of sheet copper was attached to the axle carrying the brass wheel. The edge of the copper disk was amalgamated, and its lower portion dipped into a trough of mercury, thus always securing a good contact. When the current was made to enter the wheel in other ways that were tried, as, for example, through a second spring, it was sometimes found that the resistance of the wheel circuit was not sufficiently low entirely to prevent the production of a sound by the derived current that under these circumstances constantly entered the receiving telephone. With the arrangement described the apparatus worked very satisfactorily, no trace of sound being audible in the receiving telephone except when the spring rested on the vulcanite strip, in which case the pitch of the fork was perfectly clear. A key was inserted so that the sound produced at one or more successive contacts could be caused to enter the ear at will.

In our first experiments we employed as a source of sound a large tuning-fork vibrating in front of a resonator and sounded by a hammer. But we found that this gave too feeble a sound for our purpose. We therefore made use of a small fork, which was set into vibration by a blow, and whose stem was lightly pressed against the disk of the transmitting telephone. A bit of wax placed at the end of the stem was found to be sufficient to prevent any chattering.

The particular form of magneto-telephone which was found most satisfactory as a transmitter, on account of its power, was a bipolar instrument having a large diaphragm, a special form made by the American Bell Telephone Company. For a receiver we found a very sensitive form of magneto-telephone made in Sweden best suited for our purpose.

The tuning-forks employed were of small size, belonging to a Valentine and Carr tonometer. In all of the experiments cited the transmitter was placed in a distant room, so that no sound could possibly reach the ear through the air.

The speed of revolution of the brass wheel was read by a speed-counter, and from this it was easy to determine the period of time during which the contact-spring rested on the vulcanite sector.

The mode of observation adopted consisted in driving the wheel at a rate such that the difference in pitch between the brief sounds heard in the receiving telephone seemed to be distinct. One of the experimenters then sounded the forks successively, presenting them one after another to the telephone, and noting the order in which they were sounded. The listener at the receiver at the other end of the line noted the pitch heard, and these estimations were afterwards compared with the order as noted by the person at the transmitter. The speed was then altered, generally being increased, and a new set of experiments undertaken. In some cases, owing to bad transmission or for other causes, the listener felt uncertain whether the decision noted was correct, and in such cases the result was marked as doubtful.

In the first series of experiments only two notes were compared, which were an octave apart; one, C_3, of 256 vibrations; the other, C_4, of 512 vibrations.

The following figures will illustrate the general character of the results. The line marked "T" indicates the order in which the forks were actually sounded. The line "R" indicates the sound as noted by the listener at the receiving telephone. The number of complete vibrations of the lower note transmitted was 0.88; of the higher, 1.76. The doubtful estimations are followed by an interrogation mark.

TABLE I.

T.	C_3	C_3	C_4	C_3	C_3	C_3	C_4	C_3	C_3	C_4	C_4	C_4
R.	C_3	C_4	C_4	C_3	C_3	C_4	C_4	C_3	C_3	C_4	C_4	C_3

TABLE II.

T.	C_3	C_4	C_3	C_3	C_3	C_4	C_4	C_4	C_3	C_4	C_4	C_4
R.	C_3	C_4	C_4?	C_3	C_3	C_4	C_4	C_3?	C_3	C_4	C_4	C_3

In the first of the above series it will be seen that three estimations were wrong, nine right, none doubtful; that is, 25 per cent were wrong, 75 per cent right. In the second series one estimate was wrong, two were doubtful, and nine correct; that is, 8.3 per cent were wrong, 16.7 per cent doubtful, and 75 per cent correct.

The following tables give a synopsis of results reached with the C_3 and C_4 forks. Except in a very few cases, twelve successive sounds were transmitted. The calculated duration of the sound is in all cases given in terms of the vibration period of both notes. The percentages are given to the nearest whole number. The first column contains the serial number of the experiment; the second (I), the percentage of incorrect estimates; the third (C), the percentage of correct estimates; the fourth (D), the percentage of doubtful estimates; the fifth (L) and the sixth (H), the duration of the sound in terms of the period of the lower and higher notes respectively. The rates are always expressed in complete vibrations.

TABLE III.

Forks C_3 (256 v.), C_4 (512 v.).

No.	I.	C.	D.	L.	H.
1	33	50	17	0.88	1.76
2	25	75	0	"	"
3	8	92	0	"	"
4	8	75	17	"	"
5	0	100	0	"	"
6	0	100	0	"	"
7	0	100	0	0 80	1.60
8	8	92	0	"	"
9	0	100	0	0.73	1.46
10	0	100	0	"	"
11	17	75	8	0.52	1.04
12	42	58	0	"	"
13	27	64	9	0 42	0 84
14	50	42	8	"	"
15	33	67	0	"	"

The following results were obtained with intervals other than the octave.

TABLE IV.

Forks C_3 (256 v.), G_3 (384 v.).

No.	I.	C.	D.	L.	H.
16	25	75	0	0 73	1.10
17	17	83	0	"	"
18	9	83	8	"	"
19	0	100	0	"	"
20	17	75	8	0.41	0.62
21	25	67	8	"	"

TABLE V.

Forks C_3 (256 v), E_3 (320 v.).

No.	I.	C.	D.	L.	H.
22	33	50	17	0.40	0.50
23	42	58	0	"	"

In the sets of experiments Nos. 22, 23, the contact-spring failed to give even pressure; and it was noticed that the sound was very badly transmitted at certain times, which corresponded with those at which some of the erroneous estimates were made.

TABLE VI.

Forks C_3 (256 v.), C_3 (260 v.).

No.	I.	C.	D.	L.	H.
24	58	25	17	0.40	0.41
25	25	75	0	"	"

It appears from the results given in the preceding tables that even with as small a fraction as $\frac{42}{100}$ of a vibration of the lower fork and $\frac{84}{100}$ of a vibration of the higher fork, when these had an interval of an octave, it was possible to distinguish one note from the other; and when the duration of the tone was greater, but still much less than two complete vibrations of the higher note, the distinction became easy. Nor was the distinction possible merely because of the possession of a clearly defined pitch by the higher note alone, whose period was shorter, so that a greater number of vibrations entered the ear in the time during which the circuit was completed through the telephone; which, it might be surmised, would enable one to distinguish it from the lower note even in the absence of any clearly defined pitch for this latter. On the contrary, the ear always recognized the existence of a distinct pitch with each note, even with the shortest duration of tone which was employed in the experiments; but, as would be expected, the ability to determine with certainty which of the two notes heard successively was the higher in pitch diminished as the duration of the sound diminished, and also as the interval between the two notes became less. The results given in No. 24, Table VI., are curious, and at the time they were reached seemed to be due to a misjudgment as to which of the tones was the higher at the beginning of the experiment. Series No. 25 was made immediately afterwards; but the notes of the forks were carefully listened to separately, in order, if possible, to fix the pitch of each in the mind. As a result three fourths of the estimates were correct.

In another series of observations several forks were struck irregularly, and an attempt was made to state which fork of the set used was heard. The listener knew what were the forks composing the set.

With forks C_3, E_3, G_3, C_4, the results given in Table VII. were reached. The separate series of observations are separated by horizontal lines. The table gives the name and rate of the forks used in the first two columns. In column V is given the number of complete vibrations of each fork in the time during which the sound lasted in the particular experiment referred to; in column O, the number of times each fork was sounded; and in column P, the percentage of correct estimations.

TABLE VII.

Note.	Rate.	V.	O.	P.
C_3	256	2.4	8	100
E_3	320	3.0	13	85
G_3	384	3.6	11	73
C_4	512	4.8	6	83
C_3	256	1.3	9	77
E_3	320	1.6	14	64
G_3	384	2.0	16	69
C_4	512	2.6	7	71
C_3	256	1.2	10	80
E_3	320	1.5	16	62
G_3	384	1.8	15	80
C_4	512	2.4	9	77
C_3	256	1.0	22	64
E_3	320	1.3	21	57
G_3	384	1.5	22	84
C_4	512	2.0	11	82
C_3	256	1.0	14	62
E_3	320	1.3	37	57
G_3	384	1.5	18	88
C_4	512	2.0	8	87
C_3	256	0.9	28	68
E_3	320	1.1	36	64
G_3	384	1.4	27	63
C_4	512	1.8	9	100
C_3	256	0.9	25	72
E_3	320	1.1	34	65
G_3	384	1.4	31	71
C_4	512	1.8	14	85

Table VIII. contains the results of similar observations made upon various series of notes.

TABLE VIII.

Note.	Rate.	V.	O.	P.
C_3	256	1.8	21	62
D_3	288	2.0	14	57
E_3	320	2.3	22	73
F_3—	340	2.4	24	71
G_3	384	2.7	22	64
A_3—	424	3.0	20	80
C_3	256	0.4	30	73
D_3	288	0.5	28	78
E_3	320	0.5	18	83
G_3	384	0.6	21	76
C_3	256	0.4	24	54
D_3	288	0.5	18	66
E_3	320	0.5	23	52
C_3	256	0.4	27	81
D_3	288	0.5	31	68
C_3	256	0.3	48	85
D_3	288	0.3	58	72
C_3	256	0.25	42	81
D_3	288	0.28	40	72

With the exception of the last three comparisons, which are inserted in this place because they were made in immediate connection with the preceding ones in the same table, the experiments whose results are given in Tables VII. and VIII. involve a more serious difficulty in estimation than do those previously considered; since, instead of having to decide merely which of two notes is the higher, it is necessary to determine the musical relation of the various notes in the set sounded. Nevertheless, even with the shortest observed duration of the sound, the uniform preponderance of correct over incorrect or doubtful judgments is altogether too great to be the result of chance.

Moreover, even when the ability to determine which was the higher of two notes was lost, with briefer durations of the sound than those recorded in the tables, there was always a clear difference in the pitch of the two notes; that is, they did not seem like the same sound.

It will of course be observed that, with the method used by us, the element of memory enters, since the pitch of each sound must be carried in the mind. With a direct comparison of the sound heard through the telephone line with that given by a tuning-fork sounded by the observer at the receiving end, it is probable that a still larger percentage of results would be correct. This remains, however, to be actually proved by experiment.

It will also be noticed from the tables that in some cases it seems easier to judge correctly when the two tones make a small interval with each other than when they make a greater one. For example, see the comparisons of C_3 and D_3 in Table VIII. That this is true when the greater interval is an octave might well be expected from the well known liability to confuse notes of this interval; but it is true of notes of other intervals which are not likely to be mistaken for each other.

It is our intention to extend these observations to briefer and longer durations of the sound, and to ascertain what number of vibrations is necessary to recognize the different musical intervals when these are entirely unknown beforehand. To obtain louder sounds it may be possible to use a microphone, although we have avoided this because of the great liability to disturbance of such a transmitter when strong vibrations actuate it. It has also occurred to us that we may use a sinusoidal electrical wave, generated by a peculiar form of alternating dynamo machine, especially devised for the production of such a current by Mr. F. A. Laws, of the Rogers Laboratory. This will give a very loud and at the same time very pure tone. We also intend to study the comparative accuracy of estimation when each sound is heard only once, as in the observations detailed in this paper, with that which is obtained when the sound is repeated two or more times.

The question may be raised, regarding the method employed by us, whether the sound given out by the diaphragm was really of as brief duration as we have assumed it to be. It might be questioned whether the vibration of the diaphragm was not in fact prolonged; so that while the duration of the electric current was, for example, considerably less than the time occupied by two complete vibrations, yet more than two complete sound-waves were actually produced.

Of course, the instant the diaphragm ceases to be actuated by the electro-magnet of the receiving telephone, it will begin to assume its natural rate of free vibration; but how minute a fraction of a second will elapse before it ceases to move at substantially the rate impressed upon it might seem doubtful. But under the circumstances of many of our experiments, in which the duration of the current was from less than one half of a vibration up to one vibration, it certainly is not possible that the vibration should continue without entire change of rate and form for from four to eight times the duration of the forced vibration, which would have to be the case in order to have two complete sound-waves produced.

Furthermore, the damping effect of the magnet upon a telephone diaphragm is such as to prevent more than a very slight amount of persistence of vibration of any kind whatever. This is shown by the facts that the natural note of the diaphragm of a magneto-receiver is never perceived in the ordinary use of the instrument, and that the quality of the sound heard at the receiver is substantially the same, although wide variations may be made in the dimensions of its diaphragm. And if the after-tone of the diaphragm persisted after each pause sufficiently long to produce a recognizable sound of definite pitch, say for the period of two complete vibrations, this would necessarily be noticeable in the actual operation of the instrument, — an effect which is not observed in practice.

Still further, in none of our experiments was there any note observed which corresponded in pitch to the natural note of the diaphragm, — a note whose pitch was so high that it could not have failed to impress itself upon our attention had it been present to any material extent.

These observations seem to show that with ordinary telephone currents there is no material vibration of the diaphragm of the receiver after the forced vibration has ceased. With a stronger current we might expect a certain continuance of the free vibration. What undoubtedly occurs is, that as soon as the electrical undulations cease to act on the receiver, its diaphragm begins to move at a different rate, passing to its free rate of vibration with great rapidity, and assuming this rate unless sooner brought to rest by acoustic and magnetic damping. This action would probably produce a noise of constant pitch, and distinct from the sound of the transmitting tuning-fork.

But although for these reasons it appears extremely unlikely that the diaphragm could continue to vibrate with its rate substantially unchanged for more than a very minute fraction of a vibration, it nevertheless seemed desirable to ascertain by actual and direct experiment whether this is the case.

For this purpose the following apparatus was devised. A Lissajous comparator, with its vibration maintained electrically, was employed in the usual manner to study the motion of a very minute glass bead mounted upon the diaphragm of a magneto-receiver, through the coils of which was carried an alternating current. The glass bead was illuminated by sunlight or the electric arc. The rate of the fork was 128 complete vibrations per second. The alternating current could be caused to flow through the telephone coils for a definite time by the same circuit-making wheel which was used in the experiments already described. As we desired to use a far stronger current than that produced by the transmitting telephone, we made use of the alternating current from a transformer excited by a Thomson-Houston alternating current machine, making 128 complete alternations per second. The strength of the current through the coils was varied by a set of resistances made of incandescent lamps from a maximum of about 100 milliampères to a minimum of about 50 milliampères, an amount vastly in excess of any telephone current. When the circuit-making wheel was at rest and in the proper position the curves of Lissajous were clearly seen. The motion of the bead was very nearly a simple harmonic one, so that the curves observed were ellipses, passing into the limiting oblique straight lines. Difficulty was met with from variations in the rate of alternation of the current, arising from very slight variations in the speed of the dynamo machine, so that it was necessary to utilize such moments as were found to be available when the steadiness was sufficient. If the circuit-making wheel is in motion, it is clear that the appearance of the curve seen will depend upon the duration of the make, or rather upon the duration of the motion of the telephone diaphragm. If the harmonic motion of the diaphragm persists for a period equal to one complete vibration of the fork of the comparator, — or, more strictly, for a period somewhat longer than this, and depending upon the relative phase of the two vibrations when the current begins to flow through the telephone, — it is evident that the curve should be a complete ellipse; but if the harmonic motion of the diaphragm lasts for a less time, then only a portion of an ellipse can be seen; and this will necessarily be deformed, as the curve must begin and end on the same vertical line; which is, of course, the vertical line given by the illuminated bead, as seen through the microscope of the comparator when no current is passing through the telephone.

The method has not yet been sufficiently perfected to give accurate quantitative results; but with the rate of alternation as stated, viz. 128 per second, and with the strong current used, in some cases over 500 times as great as the ordinary current furnished by a magneto-transmitter, with a calculated duration of current of from $\frac{1}{512}$ of a second to $\frac{1}{256}$ of a second, in no case was a complete ellipse observed. In many cases the duration as determined from the curve appeared to be substantially the same as the calculated amount; and when there was a prolongation of the motion it was evident from the character of the curve that this was due to free vibration of the diaphragm.

From these results it would appear that the method used by us is not open to the objection referred to, and that there is really no material prolongation of the harmonic motion of the diaphragm of the telephone after the electric undulations have ceased to actuate it. Moreover, with the very weak current used in the transmission of the sounds of the tuning-forks in our experiments, any such prolongation, if it existed, would of course be far less than with the strong current used in testing the point immediately under consideration. The effect of an increased rate of alternation ought to be studied, but the damping effect of the magnet would be greater at higher rates.

Some other experiments were made, however, with a current having 256 complete alternations per second, and of a rigorously simple harmonic form; but much difficulty was experienced in securing sufficiently equable driving with such means as were available at the time of the experiment, so that further work in this direction had to be postponed until better conditions for steadiness could be secured.

The improbability of any prolongation of the sound vibrations within the ear itself has been shown by Herroun and Yeo.*

A few experiments were made by us with a view of gaining some information regarding the free vibration of the telephone diaphragm after it was pulled to one side and suddenly released. For this purpose a direct current was substituted for the alternating current used in the experiments already described. The strength of the current was substantially the same as before. When the circuit-making wheel completed the circuit, the diaphragm was suddenly drawn toward the magnet and released quickly, when the circuit was broken. With a duration of current of about $\frac{1}{512}$ of a second the free vibration seemed to last for about the same period. With a duration of current of $\frac{1}{256}$ of a second, the free vibration lasted from $\frac{1}{512}$ of a second to $\frac{1}{256}$ of a second. With a duration of current of $\frac{1}{128}$ of a second, the free vibration often lasted as long as $\frac{1}{128}$ of a second. Under these circumstances the curve frequently showed clearly the character and rate of the free vibration of the diaphragm.

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* Proc. Royal Soc., Vol. L. p 318.

It is uncertain whether it will be possible to study the duration of the motion of the diaphragm by employing such currents as are ordinarily used in telephony, as the effect of these is so slight. In such a research it may prove advantageous to employ two telephones in circuit, each furnished with a mirror, and giving a fragment of a Lissajous curve when a beam of light is successively reflected from the mirrors, the momentary current being sent through the telephones by the circuit-making wheel; or a telephone with an objective carried by its diaphragm might be substituted for the fork of the comparator.

Two other methods have occurred to us of investigating the subject under consideration, which we hope to be able to make use of. The first of these is to employ the wave siren of Koenig, using a disk possessing only a single undulation of the sinusoid, or a fraction of an undulation; or, for repeated sounds, an ordinary disk with only a definite fractional part of the undulations exposed to the action of the jet of air. Or perhaps the same result may be obtained by the use of a narrower slit than that ordinarily employed, so that the air jet shall cover only a portion of the sinusoid.

The second method is to employ a phonograph, on the wax cylinder of which are impressed sinusoidal undulations produced by the sound of a tuning-fork. If only a single such undulation, or portion of an undulation, is allowed to remain, after removing the others by paring away the wax, the diaphragm will necessarily execute only a single harmonic vibration, or fraction of a vibration, when the cylinder is rotated in the ordinary manner.

Rogers Laboratory of Physics,
May, 1892.

XVI.

THE TROPICAL FAUNAL ELEMENT OF OUR SOUTHERN NYMPHALINÆ SYSTEMATICALLY TREATED.

BY SAMUEL H. SCUDDER.

Presented November 9, 1892.

IT is not a little remarkable that, with the exception of Hypanartia (Vanessini) and Diadema (Argynnini), all those genera of the subfamily Nymphalinæ which are essentially tropical or subtropical, and are represented on the extreme southern border of the United States by a very few species each, (species which in many cases must be looked upon as more or less accidental visitors,) belong to a few tribes which directly follow one another between the Nymphalini and Vanessini. Nevertheless they show a great diversity of forms, and since in the systematic arrangements heretofore given they have not been so closely connected as they are here conceded to be, I have thought it well to give the following succinct treatment of them, originally planned for a Manual of our Butterflies. The account of the early stages is very largely drawn from Wilhelm Müller's "Südamerikanische Nymphalidenraupen," but this has been supplemented from various sources.

TRIBE VICTORINIINI.

Butterfly: Antennæ very slender, the club moderately stout, rather short and rather rapidly incrassated, laterally tricarinate beneath except at extreme tip. Palpi compact, slender, tapering greatly, the last joint of considerable length. Wings broad with a feeble angle at the first inferior subcostal nervule of fore wings, the hind wings crenate with a distinct lobe at the upper median nervule; cell of both wings open. Last tarsal joint with two rows of spines beneath. *Egg:* Subconical, provided with few (9–11) and rather prominent ribs, which increase slightly in height toward but not reaching the pole. *Caterpillar at birth:* Head rounded, covered with simple bristles. Trichomes of body bristle-like, in five longitudinal series on each side, pointed, and longer, some much longer, than the segments, those of the upper and lateral rows arcuate and bent forward at tip, the others straight. *Mature Caterpillar:* Head with a pair of long diverging coronal spines of uniform diameter but more or less enlarged at tip and with a few scattered papilla-seated hairs. Body with long and slender mostly pointed spines, when pointed terminating in a needle, their sides furnished sparsely with sessile needles; all ranged in three series on the sides, the lowest infrastigmatal, besides a dorsal set. Feeds on Acanthaceæ. *Chrysalis:* Rather stout and well rounded; abdomen without ridges, the basal segments moderately short, the third and fourth with several central conical spines, similar to the pointed mesothoracic and frontal tubercles, those of the abdomen sometimes obsolete; cremaster long and slender.

SYNOPSIS OF OUR GENERA.

VICTORINA. *Butterfly:* Last median branch of fore wings very strongly bowed at the base. *Egg:* ——. *Caterpillar at birth:* Trichomes relatively short. *Mature Caterpillar:* Coronal spines of head scarcely enlarged at tip. *Chrysalis:* Third and fourth abdominal segments furnished with pointed spines.

ANARTIA. *Butterfly:* Last median branch of fore wings normal. *Egg:* ——. *Caterpillar at birth:* Trichomes relatively long. *Mature Caterpillar:* Coronal spines of head clubbed at tip. *Chrysalis:* Third and fourth abdominal segments without raised spines, their place indicated by dark spots.

VICTORINA Blanchard.

Butterfly: Antennal club relatively slender, about twice as broad as the stalk. Second superior subcostal branch of fore wings long, arising before the end of the cell; second inferior subcostal branch gently bowed at the base; last median branch strongly bowed at the base, in contrast to that of the hind wings; tail of hind wings longer than broad. Fore tarsi of male not half the length of the tibia. *Egg:* See tribe; laid singly. *Caterpillar at birth:* Trichomes shorter than in Anartia. *Mature Caterpillar:* Coronal spines of head terminating in two or three tubercles which slightly enlarge its diameter. *Chrysalis:* Frontal tubercles, mesonotal tubercles, and those of third and fourth abdominal segments high, conical, and pointed, the last arranged in a transverse row on each segment. (Victoria; — name given soon after the accession of Queen Victoria.)

VICTORINA STÉLENES Linn. (Papilio lavinia Fabr.; Nymphalis steneles God.) *Butterfly:* Upper surface of wings rich dark brown, marked with greenish white in a very broad premedian band crossing the hind wings and half the fore wings, supplemented on the fore wings by four very large elongated spots in the apical half of the wing, the lowermost connected with the band and sending a tongue into the middle of the cell; midway between band and margin a row of large oval green spots, continued on fore wings as a premarginal series of unequal, round, often faint, whitish spots. Under surface pale pearly green, the limits of the bands and spots of upper surface more or less vaguely mapped in ferruginous. Expanse 100 mm. *Mature Caterpillar:* Coronal spines of head 8 mm. long, red, broadly crimson at base, whitish in the middle, and brownish at tip. Body velvety black, the spines reddish gray, a mediodorsal stripe of stiff pile, less abundant than the unequal papilla-seated pile on the sides. Feeds on Blechum. *Other stages* unknown. — S. Fla.; New Mexico; perhaps a mere straggler from the south.

ANARTIA Hübner.

Butterfly: Antennal club relatively stout, about three times as broad as the stalk. Second superior subcostal branch of fore wings short, arising beyond the end of the cell; second inferior subcostal branch retroarcuate at base; last median branch normal, as in hind wings; tail of hind wings broader than long. Fore tarsi of male much more than half as long as the tibia. *Egg:* See tribe; laid singly. *Caterpillar at birth:* Trichomes longer than in Victorina. *Mature Caterpillar:* Coronal spines of head clubbed at tip. *Chrysalis:* All the tubercles, including the frontal and mesonotal, obsolescent, those of the abdominal segments obsolete, their place marked only by pigment. (ἀνάρτιος, incongruous; in allusion to its great difference in markings from its fellows ?)

ANÁRTIA JÁTROPHÆ Linn: *Butterfly:* Upper surface of wings, except upper outer portion of fore wings, washed centrally with white, with two broad, crenated black-edged fulvous bars across cell of fore wings, an interrupted brown median line across both wings (in the hind wings formed of crescents), and three partial similar lines across the basal half of hind wings, besides a pair of slender brown crescentic premarginal bands on both wings, on a light fulvous base, and moderately large round black spots in the lower median interspace of both wings and the lower subcostal interspace of fore wings. Under surface whitish lilac, with somewhat similar markings, the fulvous inclining to ferruginous. Expanse nearly 60 mm. *Egg* and *Caterpillar at birth:* Unknown. *Mature Caterpillar:* Black, the front of the first thoracic segment, the prolegs, and the base of many of the spines more or less ochraceous. Feeds on Lippia. *Chrysalis:* Smooth and wholly black, except that the borders of the antennal cases and the stigmatal fissures are whitish, and the cremaster is somewhat ochraceous at base. — Texas, S. Florida.

TRIBE EPICALINII.

Butterfly: Antennæ exceedingly slender, the club slender, nearly always elongate and then very gradually incrassate, feebly unicarinate beneath, the carination concealed when the club is elongate by the infolding of the under surface. Palpi compact, tapering, subcompressed and rather elongate, the last joint moderately long. Wings simple, usually broad, the hind wings well rounded, entire or feebly crenulate; cell of hind wings open, of fore wings open or closed by a feeble sinuate vein. Last tarsal joint with two rows of spines beneath. *Egg:* Short, subconical, provided with few (10–11) not very prominent ribs which increase very slightly in height toward without reaching the pole. *Caterpillar at birth:* Head simple, subtriangular. Trichomes of body bristle-like, very short and apically knobbed, arranged in five longitudinal series on each side, three above the spiracles. *Mature Caterpillar:* Head subquadrate, supporting a pair of excessively long, widely diverging subequal horns, armed with more or less whorled spinelets. Body armed with long, ranged, corneous, sparsely aculiferous spines, occasionally furnished with one or two spinelets, and always crowned by an independent needle, some of the spines occasionally reduced to warts; there are a dorsal series, and two other pairs above the spiracles, all the developed spines of nearly the same length. Feeds on Sapindaceæ, Euphorbiaceæ, and Urticaceæ. *Chrysalis:* Smooth, somewhat depressed, especially on abdomen, which tapers rapidly and has no ridges; a slight mesothoracic carina, sometimes produced to a point, prominent wing tubercles and short conical frontal tubercles; cremaster broad.

SYNOPSIS OF OUR GENERA.

EUNICA. *Butterfly:* Two superior subcostal nervules arising in the fore wings before the end of the cell, which is closed; costal and median veins much swollen at the base. *Mature Caterpillar:* Coronal horns of head with a very few opposed spinelets. Body subcylindrical.

DIÆTHRIA. *Butterfly:* Eyes pilose. First superior subcostal nervule of fore wings arising at end of cell, which is open; costal and median veins moderately swollen at base. *Mature Caterpillar:* Coronal horns of head with a few spinelets arranged in whorls. Body stoutest in the middle.

MESTRA. *Butterfly:* Second superior subcostal nervule of fore wings arising at end of cell, which is closed; only the costal nervure swollen at base. Fore tarsi of male excessively short. *Mature Caterpillar:* Unknown.

EUNICA Hübner.

Butterfly: Antennal club long and slender, very gradually incrassate. Eyes naked. First and second superior subcostal branches of fore wings arising before the end of the cell; cell closed by a feeble vein; both costal and median veins much swollen at the base. Fore tarsi of male as long as the tibia. *Egg* and *Caterpillar at birth:* Distinctive features undescribed, the eggs laid singly. *Mature Caterpillar:* Coronal horns of head curved at tip, furnished with only a very few opposed spinelets. Body of nearly equal thickness throughout, the developed spines ending in a straight thorn. Feeds on Sebastiana (Euphorbiaceæ). *Chrysalis:* Mesothoracic carina feebly developed. (Eunice, a Nereid.)

EUNÌCA MÓNIMA Cram. (Nymphalis myrto God.; Cybdelis hyperipte Edw. nec Hübn.; E. modesta Bates.) *Butterfly:* Upper surface of wings soft blackish brown, the apical half of the fore wings black, the whole with exceedingly faint purplish reflection; two distant straight oblique rows of rather small more or less obscure whitish spots cross the apical black field of fore wings, the inner of three, the outer of two spots. Under surface gray-brown, the hind wings and apex of fore wings with a faint bluish tinge, the markings of the fore wings repeated, but the black not reaching the apex, the hind wings crossed by three wavy dark brown lines, the outer submarginal, and between it and the median line a transverse series of very faint, finely brown-edged ochraceous ocelli with minute black pupils, that in the upper subcostal interspace blue-pupilled. Expanse 45 mm. *Early stages:* Unknown. — Texas, Florida.

DIÆTHRIA Billberg.

Butterfly: Antennal club rather short, rather rapidly incrassate. Eyes briefly and sparsely pilose. First superior subcostal nervule of fore wings arising at the end of the open cell; costal and median veins moderately swollen at the base. Fore tarsi of male as long as the tibia. *Egg* and *Caterpillar at birth:* Distinctive features undescribed, the eggs laid singly. *Mature Caterpillar:* Coronal horns of head straight, with stellate or whorled arrangement of the few spinelets. Body enlarged in the middle and tapering, especially behind, many of the developed spines ending in two unequal thorns directed forward and backward. Feeds on Trema (Urticaceæ). *Chrysalis:* Distinctive features undescribed. (*δίαιθρος*, quite fine.)

DIÆ̀THRIA CLÝMENA Cram. (Callicore janeira Feld.; C. clymena var. meridionalis Bates.) *Butterfly:* Upper surface of wings rich velvety black marked with bright blue, the fore wings crossed by a narrow outwardly crenate belt not reaching either margin from within middle of costal to near end of inner margin, where the scales are metallic; and by a brief preapical slender transverse line; the hind wings with a premarginal, rather narrow, equal band not quite crossing the wing. Under surface of fore wings crimson on more than the basal half, black beyond, crossed near tip by two strongly arcuate, inferiorly tapering white stripes, the inner the broader; hind wings velvety black, the costal margin marked by carmine, the disk with two large irregular double white rings partially encircled by two common larger ones, the outer almost marginal. Expanse 40 mm. *Egg:* Broad at base, nearly hemispherical, with 10–11 vertical ribs and very delicate cross lines; laid singly. *Caterpillar at birth:* Head simple and with body green. *Mature Caterpillar:* Head green, the coronal horns excessively long, straight, brownish green, green posteriorly, having four or five equidistant whorls of spinelets. Body yellowish green with yellowish subdorsal stripes and white papillæ. Length 22 mm. Feeds in Brazil on Trema micrantha. *Chrysalis:* Velvety green on back, pale green below; a white and brown stripe follows the alar ridges, continued on the abdomen as an infrastigmatal stripe; white points occupy the position of the subdorsal spines of the caterpillar. — Has been known to occur once in S. Florida.

MESTRA Hübner.

Butterfly: Antennal club long and slender, gradually incrassate. Eyes naked. Second superior subcostal nervule arising at the end of the cell, which is closed by a slender vein; costal nervure very much swollen at the base. Fore tarsi of male excessively short. *Early stages:* Unknown. (Derivation obscure.)

MÉSTRA AMYMÒNE Ménétr. (Cystineura dorcas Edw.) *Butterfly:* Upper surface of fore wings white, the base and costal and outer margins light brown, the costal margin with a triangular tooth of brown beyond the cell, the outer margin more broadly bordered above than below and often tinged next the edge with yellow; hind wings fulvous yellow outwardly, the extreme margin brown, pale gray at base with a median and more obscurely a prebasal transverse white band broadest on the costal margin. Under surface ochraceous yellow with the white markings of the upper surface repeated, the prebasal band of the hind wings distinct and brown-edged, the median band more or less broken into unequal brown-edged sometimes confluent roundish spots. Expanse 44 mm. — Texas, September.

TRIBE GYNÆCIINI.

Butterfly: Heavy bodied. Antennæ moderately stout but long, the club slender, elongate, gradually incrassate. Palpi compact, moderately slender, tapering, the last joint rather short. Wings simple, subtriangular, broad, especially the hind pair at its subtruncate outer margin, entire, the hind pair sometimes with a small anal lobe; cell of both wings closed by a slender vein. Last tarsal joint with two rows of spines beneath. *Egg:* Conical, with about 11 very prominent vertical ribs nearly reaching the pole. *Caterpillar at birth:* Trichomes of body shorter than the segments, straight, delicately clubbed at apex, finely toothed. *Mature Caterpillar:* Head thorny, crowned by a pair of thorny spines longer than the head and similar to those of the body, which are long, corneous, surmounted by a whorl of spinelets as important as the terminal thorn, in ranged series, one mediodorsal as important as the others. Feeds on Urticaceæ. *Chrysalis:* Slender and elongate, straight, tuberculate, especially at anterior extremity, bearing a rude resemblance to that of Papilio s. s. or Thais, some of the tubercles of the laterodorsal series prominent and directed downward.

SMYRNA Hübner.

Butterfly: Body very robust. Eyes naked. Second superior subcostal nervule of fore wings arising before the tip of the cell, the third well before the middle of the wing and extending to the very apex; lowest median nervule of hind wings produced to a short lobe. *Caterpillar:* Only the second stage is known, showing it to be similar to that of the tropical Gynæcia. (σμύρνα, myrrh; allusion wholly obscure.)

SMÝRNA KARWÍNSKII Hübn. *Butterfly:* Upper surface of fore wings dark brownish tawny at base, black at apex, the colors separated by a straight oblique pale yellow stripe, broad above, tapering below, its inner limit just bordering the cell; three large roundish white spots in a similarly oblique row just before the apex; hind wings dark brownish tawny, margined broadly above, narrowly below, with black. Under surface of fore wings brown at base, followed by a transverse broad oblique slightly arcuate pale yellow band, beyond black, separated from the mottled apex by the repetition of the spots of upper surface; hind wings light gray brown, the basal half or more crowded with concentric, more or less oval but irregular rings of blackish brown, centring, where most regular, in the costo-subcostal and medio-submedian interspaces, the whole outwardly limited by an exceedingly irregular indented line, having its farthest extension in the costo-subcostal interspace and on the submedian nervure; outer portion clouded with dark brown in inverted lunules, centrally marked with two large and two slightly smaller and brighter slightly ovate multicolored ocelli. Expanse 90 mm. *Early stages:* Unknown. — Texas, New Mexico; accidental.

TRIBE COEINI.

Butterfly: Very heavy bodied and large, with very short abdomen. Antennæ naked throughout, stout but long, the club not much enlarged, subcylindrical, elongate, gradually incrassate, both club and stalk delicately bicarinate on the inner lower surface. Palpi very compact but not slender, rapidly tapering and pointed, appressed, the last joint short and rapidly tapering. Wings large and broad, the apex of the fore wings broadly produced, the hind wings with the outer margin rounded subtruncate with or without tails; cell of both wings open or closed; penultimate superior subcostal nervule of fore wings hugging the main stem for half its length and then suddenly divergent. Last tarsal joint with two rows of spines beneath. *Egg* and *Caterpillar at birth:* Unknown. *Mature Caterpillar:* Head with a pair of short prickly coronal horns. Body armed with ranged thorns having a preapical whorl of spinules; besides the dorsal series there is but a single row on either side above the spiracles, so that the sides of the body are widely exposed. Feeds on Urticaceæ. *Chrysalis:* Rather elongate, compressed, with a dorsal keel and a series of stiff dorsal thorns, preapically whorled with spinules, on the principal abdominal segments; frontal tubercles formed of rather long, cylindrical curved projections; cremaster broad but pointed.

SYNOPSIS OF OUR GENERA.

Coea. *Butterfly:* Cell of both wings closed; hind wings tailed. *Early stages:* Unknown.

Historis. *Butterfly:* Cell of both wings open; hind wings entire. *Mature Caterpillar:* Head with enormously clubbed coronal appendages. *Chrysalis:* Dorsal spines of abdomen on anterior edge of segments, and 4–5 rayed at apex.

Coea Hübner.

Butterfly: Antennæ less than half as long as the fore wings; fore wings with the cell closed and the third superior subcostal nervule arising at or beyond the middle of the wing; hind wings with cell closed and the upper median nervule prolonged to a slender tail. *Early stages:* Unknown. (κοέω, i. e. one who perceives; see the next genus.)

Coëa acherónta Fabr. (Pap. cadmus Cram.; Pap. pherecydes Cram.) Upper surface of fore wings tawny fulvous at base, separated from the black apex and outer margin, sharply above, vaguely below, by a line which crosses the outer part of the cell obliquely to the centre of the upper median interspace and then zigzags toward the lower outer angle; the black apex has six subquadrate or triangular white spots, four in an oblique series and two beyond, irregularly placed and unequal; hind wings rich dark brown, the basal half with fulvous hairs. Under surface of various shades of brown, enlivened by areas of blue, lilac, and nacreous, the basal half slightly the darker and limited outwardly by a strongly and irregularly crenulate black line, which on the hind wings sends a long loop outward along the upper side of the submedian nervure; other large subocellate black-edged markings occur in the basal half of the wings, a broad submarginal sprinkling of dark brown and lavender scales before the tail of the hind wings, and a nearly straight dark ferruginous cloudy streak across the middle of the outer half of both wings starting from a subapical white spot on the costal margin of the fore wings. Expanse 85 mm. — Texas, New Mexico; accidental visitor.

Historis Hübner.

Butterfly: Antennæ half as long as the produced fore wings; these with the cell open and the third superior subcostal nervule arising well before the middle of the wing; hind wings with the cell open and no tail. *Egg* and *Caterpillar at birth:* Unknown. *Mature Caterpillar:* Coronal spines of head strongly clubbed apically. Spines of body terminating in only three spinelets; transversely striped on the sides with three or four stripes to each segment. *Chrysalis:* Dorsal ridge terminating on the abdomen at the posterior limit of the saddle; alar ridge subobsolete; dorsal spines at anterior edge of abdominal segments ending in a whorl of four or five spinelets. (ἵστωρ, one who knows; see preceding genus: allusion obscure.)

Hístoris orìon Fabr. (Aganisthos o. Bd.-LeC.; Pap. odius Fabr.; Pap. danaë Cram.) *Butterfly:* Upper surface of wings blackish brown, the hind wings more or less fulvous at base, the fore wings with a very large bright fulvous patch occupying almost the whole of the basal half of the wing, and extending as a blunt subtriangular offshoot into the middle of the distal half nearly to the margin; a small preapical ovate whitish spot next costal margin. Under surface rich dark olive-brown, crossed just within the middle by a broad finely black and blue edged lighter band which broadens toward each border, and somewhat similar more basal markings, besides scattered lilac fleckings next the middle of the outer border, marginal and broad on the fore wings, narrow and submarginal on the hind wings; other fainter clouded lines. Expanse 120 mm. *Mature Caterpillar:* Clubbed coronal horns of head beset with thorns. Body green, with dark transverse stripes, of which the anterior of each segment is broader and darker than the others, which are more or less interrupted. Length 75 mm. Feeds on Cecropia. *Chrysalis:* Frontal tubercles granulated; joints of distal half of antennal cases each with a small conical tubercle. Body longitudinally striped with darker and lighter colors. Length 55 mm. — S. Florida; rare and accidental visitor.

Tribe TYMETINI.

Butterfly: Rather slender bodied, with short abdomen. Antennæ long and slender, feebly scaled, the club rather slender, elongate, gradually incrassate; both club and stalk bicarinate beneath interiorly. Palpi rather slender and elongate, triquetral, apically tapering to a blunt point, the last joint rather short and not very slender. Wings ample, the fore pair broadly produced at the apex, sometimes falcate, the hind wings subtriangular with a distinct anal lobe and an elongate blunt tail at the upper median nervule; cell of both wings open; subcostal and median veins of hind wings nowhere approximate. Legs delicate and short, the under surface of last tarsal joint with two rows of spines, the others with four. *Egg* and *Caterpillar at birth:* Unknown. *Mature Caterpillar:* Coronal spines of head exceedingly long, briefly and abundantly aculiferous, slender, tapering. Body armed only with a dorsal series of erect tapering filaments on a few segments. Feeds on the Fig family and Anacardiaceæ. *Chrysalis:* Not very elongate; frontal projections consisting of long slender tapering filaments, similar ones (flexible ?) crowning the basal wing tubercles, and still others of varying length forming a dorsal series on the abdomen.

MARPESIA Hübner.

Butterfly: Body small for the ample wings. Fore wings apically produced, often falcate; second superior subcostal nervule arising at the end of the cell, the third far toward the tip of the wing; hind wings with very long tails. Fore tibia and femur of male of equal length, the tarsus not half so long; fore tibia of female much shorter than either femur or tarsi. *Mature Caterpillar:* The dorsal filaments are arranged on alternate abdominal segments beginning with the second, the last on the eighth being curved backward apically (much like the anal horn of a hawk-moth caterpillar) and a little longer than the others. *Chrysalis:* Compact, laterally compressed, with dorsal and anal carinæ; head very broad, bearing outwardly a pair of slender filamentous processes much like those of the caterpillar; and similar processes appear on the mesonotal and basal wing tubercles as well as a dorsal series on the second to the eighth abdominal segments, the first abdominal, the thoracic, and the cephalic filaments longer than the rest; cremaster bent downwards, the surface of attachment elongate, parallel to venter. (Marpesus, nom. propr.)

§ MARPESIA proper. *Butterfly:* Costal margin of fore wings very strongly arched; hind wings emarginate at upper outer angle, but yet with anterior portion longer than posterior part of fore wings and about as long as their own inner margin apart from the lobes; tails subspatulate. Prevailing colors tawny. *Caterpillar* feeds on Ficus and Anacardium.

MARPÈSIA PÈLEUS Sulz. (Pap. thetys Fabr.; Pap. petreus Cram.; Timetes eleucha Edw.) *Butterfly:* Upper surface of wings tawny, crossed by three common, straight, slender black or dark ferruginous stripes, the inner not reaching the margin of either wing, subequidistant, but the outer two converging on the hind wings and bent abruptly outward at the subcostal nervure on the fore wings, the outer double on the hind wings; the cell of the fore wings is crossed by another feeble stripe between the inner two; the outer margin is more or less obscured with blackish brown especially on the hind wings, where the outer stripe terminates in a pair of more or less obscure transversely oval ocelli ringed with white. Under surface dead leaf (♂) or livid (♀) brown, much enlivened by lighter and darker clouds, the stripes of the upper surface indicated more by light than by dark lines, excepting the most conspicuous middle stripe of the hind wings, which is also light-edged inwardly; large faintly indicated obsolescent ocelli follow the outer margin distantly on both wings, most distinct opposite those of the upper surface. Expanse 85 mm. *Mature Caterpillar:* Head obscure yellow, with two black vertical streaks on the face and a black ocellar spot, the coronal horns with short stiff hairs. Body reddish brown except the ventral surface and the dorsal surface from the third abdominal segment backward, which are yellow; the sides are marked in front with round black spots, some with an oblique white line through them; behind, on most of the abdominal segments, with long, oblique, generally white-edged black stripes. Length 36 mm. Feeds on Ficus and Anacardium. *Chrysalis:* White or yellow, marked with dorsal and suprastigmatal rows of pretty large black spots the whole length of the body, besides a large laterodorsal spot on each side of the mesothorax, the filaments and cremaster black. Length 20 mm. — Florida, Texas; accidental.

MARPÈSIA PELLÈNIS God. (M. eleuchea p. Hübn.; Timetes eleucha Westw.-Hew.) *Butterfly:* Upper surface of wings tawny, crossed by three inequidistant slender black or ferruginous stripes, the middle one of which is abruptly bent outward at the median nervure of the fore wings, while the outer, which is double on the hind wings, fades out on the upper part of the fore wings; the cell of the fore wings is crossed more or less distinctly by three other similar stripes; outer third of costal margin broadly bordered with black; a submarginal blackish line on both wings, slenderer on the hind pair, and a brown gray field next the margin in the median area of the hind wings enlivened by white-capped transversely oval black and gray ocelli. Under surface lighter (♂) or darker (♀) light dead-leaf brown with the stripes of the upper surface more or less obscurely repeated in ferruginous, accompanied by a series, distant from the margin, of large shadowy ocelli, at all distinct only next the anal angle of hind wings. Expanse ♂ 60, ♀ 75 mm. *Caterpillar* feeds on Ficus. — Texas, New Mexico, Florida; occasional.

§ Tymetes Boisduval. *Butterfly:* Costal margin of fore wings gently convex; upper outer angle of hind wings in no way emarginate and yet the anterior portion no longer than the posterior part of the fore wings and very much shorter than the much produced inner margin, disregarding the lobe; tails tapering or rounded apically. *Prevailing colors* dark brown. *Caterpillar* feeds on Maclura and Morus. (*τιμητής*, an appraiser of values; allusion obscure.)

Marpèsia corèsia God. (M. zerynthia Hübn.; Pap. sylla Perty.) *Butterfly:* Upper surface of wings obscure ferruginous brown at the base, deepening outwardly nearly to the border to black-brown, in which, next its outer limit, is a slender, straight, brown stripe, very faint on the fore wings; outer margin broadly ferruginous brown, the hind wings with a pair of slender submarginal blackish brown stripes, sharply angulated at the tail. Under surface with the basal half silvery white, sharply delimited, with two parallel slender ferruginous threads across it followed by a narrow, outwardly black-edged brownish red stripe, the edging deeply crenate; outer half chocolate-brown with the premarginal stripes of the upper surface repeated dully. Expanse 65 mm. *Early stages:* Unknown. — Texas, New Mexico; occasional.

Marpèsia chìron Fabr. (Megalura c. Blanch.; Pap. marius Cram.; Marpesia chironias Hübn.) *Butterfly:* Upper surface of wings brown, with four common, straight, equidistant, tapering, transverse, blackish brown stripes, the outer two curving inward on the median area of the hind wings, the whole apex of the fore wings blackish, crossed by two parallel distant series, one of three, the other of two, minute white spots, the hind wings with a pair of submarginal black stripes (blended on the fore wings) and two subocellate transverse spots above anal angle, besides a minute orange-centred longitudinally oval spot at extreme angle. Basal half of under surface dull lilac-white, with four subequidistant transverse ferruginous threads crossing it, beyond the outer of which the white is changed to very pale yellow; outer half very pale reddish brown faintly cross-striped with iridescent lilac, with a pair of slender premarginal reddish stripes; the white spots of the apex are cloudily repeated on the fore wings, the ocelli, somwehat altered, on the hind wings, and a fine black premarginal thread runs below the tail. Expanse 60 mm. *Caterpillar:* Undescribed; feeds on Morus and Maclura tinctoria. — Texas, occasional.

TRIBE AGERONIINI.

Butterfly: Antennæ very long and rather slender, the club slender, very elongate and gradually incrassate, bicarinate on the inner side and deeply sulcate between the carinæ. Palpi as in the preceding tribe. Wings ample, simple, the hind wings well rounded with subcrenulate margin; cell of both wings broad and closed. Legs moderately stout, compactly clad, the last tarsal joint with two rows of spines. *Egg:* Short barrel-shaped or rounded, with few (about 10) low vertical ribs often run together above. *Caterpillar at birth:* Trichomes shorter than the segments, apically knobbed. *Mature Caterpillar:* Head subquadrate, crowned by a pair of very long, equal or apically enlarged, widely diverging, briefly aculiferous spines. Body armed with tapering, briefly aculiferous spines of very unequal length ranged in series (one or two spines mediodorsal) most important in the upper series and toward the extremities of the body. Feeds on Euphorbiaceæ. *Chrysalis:* Slender and elongate, laterally keeled over most of the body, dorsally gently hunched on mesothorax and sometimes at base of abdomen, the frontal projections of excessive length, strongly divergent and tapering.

AMPHICHLORA Felder.

Butterfly: Antennæ long, the club long and slender, not more than twice as stout as the stalk, gradually incrassated. Wings ample, the fore wings with the costal margin faintly emarginate at the end of the long cell, the costal vein swollen, the first two superior subcostal nervules arising near together just before tip of cell, the third not far beyond it, and hugging the main vein for the first part of its course; vein closing the cell tortuous and striking the median vein well before its last forking. Fore tarsi of male with a flat mat of diverging hairs. *Egg:* Barrel-shaped, with 10 vertical ribs; laid singly or in columns. *Caterpillar at birth:* See tribe; makes a perch along a midrib with frass and covers itself with its own dung pellets which rest between the trichomes. *Mature Caterpillar:* Coronal spines of head three times as long as the face; inequality of spines of body less marked than in others of the tribe. Feeds on Dalechampia. *Chrysalis:* Relatively stout, with rather rapidly tapering abdomen and frontal horns almost half as long as the body. (ἀμφί, χλωρός, encompassed with green, i. e. a spring butterfly.)

AMPHICHLÒRA FÓRNAX Hübn. (Ageronia f. Hübn.) *Butterfly:* Upper surface of wings marbled in the most intricate fashion with black, white, brown, and cerulean blue, the black and brown appearing to form the ground color, the white occurring almost entirely on the fore wings and there forming a loose broad band of large spots running from beyond the middle of the costal border to the lower outer angle, the blue appearing as lunulate, subcontinuous transverse markings, and next the margin, especially on the hind wings, as the outer ring of large ocelli having usually a white or blue pupil; a sinuous black bar crosses the middle of the cell of the fore wings having a red spot in its lower half. Under surface of fore wings as far as middle of cell impure white, beyond black heavily spotted with pure white, the larger spots comprised in three transverse parallel bands, in each of which, especially the middle one, the spots are subequal, but the shorter outer band has one longitudinal bar greatly larger than the others in its series; the cellular bar is repeated; hind wings uniform dark brownish yellow, with a marginal series of black-capped white spots, the outer half or more of the upper three interspaces filled with elongate black and white ocellate spots, and the following three with a very small black-capped or encircled white spot near centre of its outer half. Expanse 75 mm. *Egg:* Short barrel-shaped with about 10 uniform vertical ribs, in part blended above, laid in columns of 5–10 in number. *Caterpillar at birth:* Not distinctively described; covers itself with pellets of its excrement. *Mature Caterpillar:* Dorsal spines of hind end and subdorsal thoracic spines with numerous small equal spinelets, giving them the appearance of cylindrical brushes; subdorsal and suprastigmatal yellow stripes, the former edged inferiorly with black, the latter sending oblique shoots downward and backward toward the stigmata; beneath red. Feeds in Brazil on Dalechampia triphylla, ficifolia, and stipulacea. *Chrysalis:* Either green or blackish brown, with a broad unequal whitish dorsal stripe, and an infrastigmatal white band, which continues forward along the edge of the wing-cases and unites with its opposite behind the frontal tubercles, involving also most of the ventral portion of the abdomen. — S. W. Texas; purely accidental

AMPHICHLÒRA FERÒNIA Linn. (Ageronia f. Hübn.) *Butterfly:* Upper surface of wings almost precisely as in A. fornax, with only a slightly greater preponderance of blue, and with the red spot extending also to the upper part of the cellular bar. Under surface of fore wings also the same, but the hind wings sordid white, sometimes with a faint yellowish tinge, and with the same markings, but the premarginal markings of the median area are large, very broadly white-centred, circular black spots, and in the same interspaces are traces of the proximal edging of the large ocellate spots of the subcostal area. Expanse 75 mm. *Early stages:* Unknown. — S. W. Texas; purely accidental.

XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

TRIANILIDODINITROBENZOL AND CERTAIN RELATED COMPOUNDS.

By C. Loring Jackson and H. N. Herman.

Presented November 9, 1892.

In a paper * published last year by one of us and W. B. Bentley, two forms of anilidotrinitrophenyltartronic ester were described, one of which was red and melted at 143°, the other yellow with a melting point of 122°. We have undertaken a more complete study of this subject because the existence of these two modifications, if they are really chemical isomeres, is not explained by any of the present theories of isomerism, unless indeed this should prove to be a case of an unsymmetrical nitrogen atom according to the hypothesis proposed by Hantzsch and Werner.† The anilidotrinitrophenyltartronic ester can be prepared in quantity only at a great expense of time and labor. It seemed wise, therefore, to begin our work by an examination of some related substances for similar modifications, as, if such were discovered in the case of a more accessible compound, their complete characterization could be worked out with greater ease. Unfortunately, as the new modifications obtained during these experiments were not so well marked as those already found, they could not be used to advantage for this purpose, and this work has taken so much time that the fuller study of the two forms of anilidotrinitrophenyltartronic ester could not be entered upon before the departure of one of us from Cambridge. The work contained in this paper, therefore, relates principally to the trianilidodinitrobenzol, which we have found appears in both red and yellow crystals, differing most strikingly in color and habit, but melting apparently at the same temperature, and passing from one

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* These Proceedings, Vol. XXVI. p. 67.

† Ber. d. ch. G., 1890, p. 11.

form to the other with great ease, so that it is doubtful whether they should be considered true isomeres. Nevertheless, it has seemed to us that, in the present state of our knowledge of isomeres, a description of such closely related modifications as these might be of advantage to the science, and we therefore publish our results, which we think the more interesting because the triparatoluidodinitrobenzol shows an exactly similar behavior. On the other hand, we have not succeeded as yet in obtaining such forms from the triörthotoluidodinitrobenzol, although it is possible that they may exist, but that the second modification is less stable than those of the anilido and paratoluido compounds.

In searching for isomeric forms of the trianilidodinitrobenzol, which we have done by a great number of varied experiments, we discovered a compound of this substance with chloroform having the formula $C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3$, which crystallized in blackish red well formed prisms, but lost its chloroform partially even at ordinary temperatures. A similar addition product was obtained with the corresponding para- but not with the orthotoluido compound; an attempt will be made in this Laboratory to trace the limits of this reaction.

Numerous attempts to prepare a second modification of trianilidotrinitrobenzol or of anilidotrinitrophenylmalonic ester have led to negative results without exception, as no change in the full yellow color or the crystalline form of either of these substances could be observed, but this result seems so strange in view of the occurrence of two modifications of the trianilidodinitrobenzol on the one hand, and of the anilidotrinitrophenyltartonic ester on the other, that a more careful study of these substances will be made hereafter, and the work extended to other substances, in the hope of collecting in time enough observations to determine the cause of the isomerism of the substituted tartronic ester.

Experiments with Trianilidodinitrobenzol.

In searching for isomeric forms of the trianilidodinitrobenzol we studied more carefully than before the crystallization of it from various solvents, and found that, when a mixture of benzol and alcohol was used as the solvent, it appeared in crystals of two sorts, one the nearly square prisms of an orange color like that of potassic dichromate already described, the other as yellow as potassic chromate in bladed crystals, or plates looking like flattened monoclinic prisms terminated by two planes, or less commonly with square ends, which, when the cooling took place rapidly, appeared in circular groups of little needles. These two modifications differed entirely in crystalline habit and color, and resembled strongly the yellow and red forms of anilidotrinitrophenyltartronic ester, the discovery of which had led us to undertake this work; but whereas the two esters showed a difference of 21° in their melting points (red 143°, yellow 122°), the yellow and red forms of the trianilidodinitrobenzol melted at the same temperature, 179°. To be sure, the yellow form turned red at about 140°, but there were no signs of melting, and we do not feel that such a change from yellow to orange-red is definite enough to have much significance. The yellow form was also much less stable than the corresponding form of the anilidotrinitrophenyltartronic ester, so that we have not obtained it absolutely free from the orange modification. The best way for preparing it that we found was to crystallize the orange form from a mixture of benzol and alcohol containing much benzol, when a portion of the substance usually appeared in the yellow form. On the other hand, a single crystallization of the yellow crystals from a mixture of benzol and alcohol containing but little benzol was sufficient to convert them completely into the orange prisms. As it was possible that the yellow crystals might be a compound containing alcohol or benzol of crystallization, instead of an isomere, we heated to 100° 0.3190 gr. of the best we could obtain, which had been air dried, but found that the loss was only 0.0004 gr., showing that this is not the explanation of the occurrence of this form.

The presence of a small amount of impurity seemed to be favorable to the existence of the modification crystallizing in plates, as, if a little tribromdinitrobenzol was present, crystals were obtained of this form although usually a little more orange in color than that made from pure material, and these would undergo several crystallizations before they were converted into the orange form. A sample, which we obtained accidentally, was even more stable, and owed this stability to an oily impurity, the presence of which was indicated by the low melting point, and which we finally succeeded in separating, but only after a great number of crystallizations, when the substance passed into the orange form; the amount of this impurity, however, was very small, as shown by the following analyses: —

I. 0.2522 gr. of the substance gave on combustion 0.6004 gr. of carbonic dioxide and 0.1086 gr. of water.

II. 0.2197 gr. of the substance gave 31.6 c.c. of nitrogen at a temperature of 25° and a pressure of 755.4 mm.

	Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2$.	Found. I.	II.
Carbon	65.31	64.94	
Hydrogen	4.30	4.79	
Nitrogen	15.88		15.95

The substance gave no test for bromine with a copper wire, or even when treated according to the method of Carius. As the amount of impurity is so small that we thought it could have no effect, we have used this preparation for the determination of the molecular weight of the yellow modification, which, with that of the orange prisms, was made by the method of Raoult, using benzol as the solvent, since preliminary experiments had shown that these compounds were not sufficiently soluble in glacial acetic acid.

Yellow Plates.

Substance 0.2290 gr. Benzol 10.299 gr. Depression 0°.27.

Orange Prisms.

Substance 0.2561 gr. Benzol 10.468 gr. Depression 0°.29.

From these results the following molecular weights are obtained: —

	Molecular Weight.
Yellow Plates	404
Orange Prisms	413
Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2$	441

There can be no doubt, therefore, that the substances are not polymeric. The benzol solutions obtained in the determinations were mixed with a little alcohol, and allowed to evaporate spontaneously, (the substance is deposited as a varnish from benzol alone,) when each yielded as the principal product the modification which had been originally dissolved in it, although in each case this was mixed with an insignificant amount of the other form.

From the observations given above we should infer that these two modifications of the trianilidodinitrobenzol are not true chemical isomeres, but physical isomeres, or perhaps rather that the substance is dimorphous.

We have made a great many experiments to get other isomeric forms of the trianilidodinitrobenzol, both by varying the method of preparation in every way we could devise, and by treating the orange prisms with reagents, which usually convert one stereoisomeric form into another, but have met with no forms except the two already described.

Compound of Trianilidodinitrobenzol and Chloroform.

If in crystallizing the trianilidodinitrobenzol a mixture of chloroform and alcohol was used instead of benzol and alcohol, dark red well formed short prisms were obtained entirely different from either of the forms just described. The whole of the substance could be converted into these prisms, if the solution in chloroform and a little alcohol was allowed to evaporate at temperatures from 50° to 70°. This substance, however, proved to be, not an isomere, but a compound with chloroform, since on heating some of the dry crystals with sodic hydrate and aniline a strong odor of phenylisocyanide was perceived.

Our first attempts to analyze it showed that the chloroform was given up partially at ordinary temperatures, but that to drive off the remainder it was necessary to heat to 100°. Accordingly we proceeded as follows. A quantity of the orange trianilidodinitrobenzol melting at 179° was dissolved in warm chloroform, and after the addition of a little alcohol poured into a large watch-glass to crystallize; when nearly all the chloroform had evaporated, the crystals were pressed as quickly as possible between filter paper till free from adhering chloroform, and then transferred at once to a stoppered glass tube, in which they were weighed.

I. 1.5012 gr. of the compound lost at 100° 0.3226 gr. of chloroform.

II. 1.4455 gr. of the substance lost at 100° 0.3059 gr. of chloroform.

	Calculated for $C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3$.	Found.	
		I.	II.
Chloroform	21.32	21.49	21.16

The residue was trianilidodinitrobenzol melting at 179°.

Properties of the Addition Compound of Trianilidodinitrobenzol and Chloroform. — This substance crystallizes in short thick prisms with both terminations well developed, apparently of the monoclinic system, which have a very dark brownish red color not unlike that of well crystallized potassic ferricyanide, and show a blue reflex. The chloroform is not securely held, part of it being given up even at ordinary temperatures with great rapidity, whereas heating to 100° is necessary to drive out the last traces. On this account its presence has only a slight effect on the melting point, lowering it by a variable amount not exceeding 3° or 4°. Standing with alcohol if the crystals are small, or grinding them with it if they are large, also drives out the chloroform, leaving the usual orange prismatic form, and the same effect is produced by one crystallization from alcohol. Its action with other solvents was not studied.

Triparatoluidinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_2$. — 10 grams of tribromdinitrobenzol were heated with 18 grams of paratoluidine on the steam bath for eighteen or more hours; the reddish black product was freed from the excess of toluidine by standing with dilute hydrochloric acid, followed by careful washing with hot water, and then purified by crystallization from benzol and chloroform. The substance thus obtained was not, however, triparatoluidodinitrobenzol, but its addition compound with chloroform, as was shown by the isocyanide reaction, and the following analysis of the crystals dried by pressing between filter paper.

0.9079 gr. of the substance lost at 100° 0.1798 gr. of chloroform.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2CHCl_3$.	Found.
Chloroform	19.83	19.81

Properties of Addition Compound $C_6H(C_7H_7NH)_3(NO_2)_2CHCl_3$. — This substance crystallizes in long plates terminated at each end by two planes at a rather sharp angle to each other. It has a dark brownish red color and loses part of its chloroform even at ordinary temperatures, but does not seem to be decomposed by alcohol so easily as the corresponding anilido compound.

In order to obtain the triparatoluidodinitrobenzol the preceding compound was dried at 100° until all the chloroform had passed off, and then crystallized from alcohol with a little benzol until it showed the constant melting point 197°, when it was analyzed with the following results: —

I. 0.1907 gr. of the substance gave on combustion 0.4707 gr. of carbonic dioxide and 0.1039 gr. of water.

II. 0.2580 gr. of the substance gave on combustion 0.6351 gr. of carbonic dioxide and 0.1299 gr. of water.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found.	
		I.	II.
Carbon	67.09	67.30	67.14
Hydrogen	5.18	6.04	5.59

Properties of Triparatoluidodinitrobenzol. — This substance crystallizes from a mixture of benzol and alcohol in characteristic acute rhombic plates of a very dark purplish red color somewhat like that of well crystallized potassic ferricyanide, but redder and more purple. It melts at 197°, and is nearly insoluble in ethyl or methyl alcohol; freely soluble in benzol or chloroform; sparingly soluble in acetone or hot glacial acetic acid, almost insoluble in the latter solvent when cold.

If the dark brownish red plates of triparatoluidodinitrobenzol are boiled with alcohol, the alcoholic extract deposits on cooling thread-like felted crystals of a yellow color, which change to red in the neighborhood of 180°, and melt at 197° like the original rhombic plates. We have found it impossible, however, to convert the whole of the plates into the yellow felted needles by this process. To prove that the yellow crystals did not contain alcohol of crystallization a portion of the preparation was heated to 120° until constant, when it was found that the loss was not more than would be mechanically retained by such a very spongy substance. The dried substance was then analyzed with the following result: —

0.2096 gr. of the substance gave 26.9 c. c. of nitrogen at a temperature of 27°.5 and a pressure of 758.6 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found.
Nitrogen	14.49	14.10

We should add that 0.3991 gr. of the dark red plates air-dried when heated to 100° for four hours lost only 0.0004 gr., so that this substance also is free from alcohol or benzol of crystallization. These observations show that the triparatoluido compound appears in two forms similar to those discovered with the anilido compound. Some other solvents beside alcohol convert the red form partially into the yellow, notably ether and acetone.

Triorthotoluidodinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_2$.

This substance was most conveniently prepared by adding 12 gr. of tribromdinitrobenzol to 35 gr. of boiling orthotoluidine, stirring the mixture, and allowing it to cool as quickly as possible to avoid the formation of purple dye stuff. The product was treated with dilute hydrochloric acid twice, allowing the mixture to stand for some time, and then washed thoroughly with water, after which it was purified by crystallization from benzol and alcohol, or chloroform and alcohol, until it showed the constant melting point 243°, when it was analyzed with the following result: —

0.2691 gr. of the substance gave 34 c. c. of nitrogen at a temperature of 23° and a pressure of 763.3 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found.
Nitrogen	14.49	14.31

Properties. — The substance crystallizes in rather stout pointed needles of a full red color, which melt at 243°, and are somewhat soluble in hot ethyl or methyl alcohol, less soluble in either cold; freely soluble in chloroform, acetone, or hot benzol, not very soluble in cold benzol; slightly soluble in hot ligroine. Sodic hydrate had no apparent action on it. An attempt to make a chloroform compound from it led to no result, the substance crystallized from chloroform showing no loss when heated to 120°. Nor have we succeeded in finding a yellow modification, although we have tried the methods which yielded such modifications with the corresponding compounds of aniline and paratoluidine; we think further experiments of this sort necessary, however, before we can be certain that such a modification does not exist. The high melting point and the observations just mentioned indicate that this ortho compound is decidedly different from the corresponding para compound.

XVIII.

PRELIMINARY COMMUNICATION ON THE HOST OF NECTONEMA AGILE, VERR.

BY HENRY B. WARD.

Presented by E. L. Mark, November 9, 1892.

IN a paper on Nectonema agile, published last June,* I endeavored to show, from purely morphological evidence, that, although known only as a free-swimming adult, this worm must be parasitic in early life. I suggested further some small fish or crustacean (Palæmonetes) as its probable host. Last October Prof. J. P. McMurrich ‡ very kindly sent me a nematode with the following description: "I obtained last summer from a Palæmonetes this nematode lying curled up in the thoracic cavity. In general form it suggests Nectonema, but lacks the lateral bands of setæ so characteristic of the free-swimming form; the parasitic habit may account for that."

The alcoholic specimen, which was in two pieces when received, measured 75 mm. in length, and 0.5 mm. in diameter, being thus longer than any adult female Nectonema hitherto reported, and surpassing even the avarage male (68 mm.) in length, so that if this parasitic worm is Nectonema, the difference in size between the sexes appears less evident than was stated in the paper cited. Externally this parasite exactly resembles the adult female Nectonema in all respects except in the entire absence of the rows of hairs which are found on the cuticula of the median lines of the latter. Cross sections show conclusively that it is a female Nectonema in approximately the same stage of development as that represented in Figure 58 (Plate IV.) of the paper already referred to. The thin body wall encloses a crowded mass of nearly developed eggs, which indicate that this specimen is quite as mature as those captured free swimming. The cuticula is clearly divided into two layers, a superficial broken stratum, of a brownish hue, and variable in thickness, which is separated by a sharp line from the underlying homogeneous bluish layer. The latter is uniform in thickness and regular in outline. These two layers are slightly separated at the median lines, and between them may be seen shreds of cuticular substance, which, to judge from tangential sections, lie in rows, and are apparently attached to the deeper layer; they are probably the hairs of the adult. From these appearances I feel justified in concluding that the outer layer is the last larval cuticula, which is ready to be cast when the nematode leaves its host, and the deeper layer is the permanent cuticula of the adult, which already bears the characteristic hairs. Since this specimen was practically as far developed as the youngest free form described in the previous paper, it was probably nearly ready to desert its host, and therefore furnishes no new evidence as to the structure of the female.

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* Bull. Mus. Comp. Zoöl., Vol. XXIII. No. 3.

‡ I desire to return my sincere thanks to Prof. McMurrich for his kindness in sending me this specimen.

The discovery of this individual seems to establish beyond question the parasitic nature of the young Nectonema, and indicates Palæmonetes as its host. On the analogy of Gordius there is some reason for supposing that Nectonema may have facultative hosts, and it may even be that Palæmonetes is only an occasional host; yet that it is normally one can scarcely be doubted in view of the maturity and perfect development of this specimen. Further, it is more probable that the development is completed in a single host than that a change of hosts occurs, and, in spite of the scarcity of the parasite, one may confidently expect, now that the attention of investigators has been directed to this host, that all stages of the development will be obtained.

The results obtained from the study of a single specimen are necessarily incomplete, and are presented in order to call attention to the host, in the hope that more material may be obtained, and also to establish the position taken in my previous paper as to the parasitic nature of the immature Nectonema. I expect to search next summer for additional material on the development, and shall be deeply indebted for any further information as to the occurrence of this nematode or its host.

Morphological Laboratory,
University of Michigan.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

XIX.

ON THE THERMAL CONDUCTIVITY OF CAST IRON AND OF CAST NICKEL.

BY EDWIN H. HALL.

Presented June 15, 1892.

IN the year 1890, having occasion to construct a thermopile of nickel and cast-iron, for experiments upon cylinder condensation in steam-engines, I wished to know approximately the ratio of the thermal conductivities of these two metals. To my surprise, I could find nothing in the books examined concerning the thermal conductivity of nickel. As to the same property in iron there was considerable information in print, but different experimenters had found very different values. I therefore determined to seek the information which I needed by experiment, following the well known method of Forbes and of Tait, — a study of the permanent gradient of temperature along a bar heated at one end, in a room of constant temperature, and of independent observations on the rate of heat emission from a bar of the same material in the same room. Forbes and Tait both used a shorter bar for the emission experiments than for the steady flow. I used the same bar for both parts of the work. My results, though claiming no great accuracy, are of some interest to the scientific world, as giving an approximate value for the thermal conductivity of nickel and of cast-iron.

I had two bars of cast-iron made, each, when finished and thinly nickel-plated to prevent rusting, about 92 cm. long and 2.52 or 2.53 cm. in width and thickness. One was of ordinary Southern cast-iron, brittle in quality, specific gravity 7.06; the other was of so called gun-iron, specific gravity 7.18, which is very much tougher than ordinary cast-iron. A number of castings were made for the gun-iron bar before one was obtained that was reasonably free from blow-holes. No such difficulty was experienced with the other iron.

To procure a nickel bar as large as the iron ones gave no small trouble. It was not to be found in the market, but some 23 lb. of commercial nickel, in various shapes, put into a new melting-pot by an obliging brass-founder, yielded, after one or two failures, a casting from which a bar 91.5 cm. long and about 2.55 cm. in width and thickness was worked out. The high melting point of nickel makes it a difficult metal to cast in the form of a long bar. A baked sand mould was finally used, and one end of it was elevated considerably above the other, in order that the whole might become filled before the metal cooled. Even with this device the success attained was not perfect, and the finished nickel bar was marred by many flaws. A little experience, however, shows that a blow-hole may be of considerable size without deserving to be counted among the more serious causes of error in the determination of thermal conductivity. Borings or cuttings from this nickel bar were analyzed by a chemist, and were found to contain *several per cent* of iron, and small quantities of other impurities, of which silicon was one. All of the nickel put into the melting-pot was represented when purchased to be fairly pure, but it was discovered too late that two pounds of it was of very poor quality, that is, contained much iron.

In each of the three bars holes about 0.55 cm. wide and about 2.3 cm. deep were bored to receive the thermometer bulbs. The length of each bar was divided into nine nearly equal parts, and one hole was bored at the middle of each part, so that the holes were a little more than 10 cm. distant from one another. Each hole was partly filled with mercury.

The thermometers used with the bars had bulbs about 0.45 cm. wide and about 2.0 cm. long. They were graduated for the purposes of this investigation on the basis of bulb-immersion only. They were not high grade instruments, and some of them were probably in error nearly 0°.5 at various points between 0° and 100°. At 100° they read from 0°.1 to 0.°3 or 0.°4 low. Above 100° the errors were more serious, — thermometer no. 8, which was sometimes used with a reading of 150° or higher, having an error of about 2° at that temperature, according to the comparison afterward made with a good thermometer lent me by Professor Holman of the Massachusetts Institute of Technology.

The conduction experiments were made in May and June, 1890, in the north side of the middle basement of the Jefferson Physical Laboratory. The bars were supported near their ends on thin wooden pillars, about 20 cm. above the top of a long wooden table. For the steady flow experiments two bars were placed in line with their ends nearly touching, and both were heated at once by the same Bunsen flame, which was protected from drafts of air by a tin casing about 38 cm. tall and 13 cm. square, pierced on two sides to admit the ends of the bars. The general temperature of the room was observed by means of six ordinary Centigrade thermometers, of which one was placed on the table near the heated bar, one about 1.25 cm. above the middle of the bar and about 30 cm. from the ceiling of the room, one near the north wall about 2.5 m. distant, another about equally distant upon a south wall, another some 10 m. away upon the western wall, and another about the same distance toward the east. During the experiments on steady flow and on rate of cooling, the thermometer lying on the table usually read about 0°.5, and the one hanging above the bar about 2°, higher than the mean of the six. The mean reading of these six thermometers differed from the mean reading of the eight thermometers used on the bars less than 0°.1, when all were placed together in water near 20°. The mean reading of the six *room* thermometers during the actual experiments upon the bars usually varied only a few tenths of a degree in an hour.

Not wishing to devote a great deal of time to the work in hand, I was content with a rather rough approximation to a state of steady flow of heat. The method followed was to take several rapid observations of all the bar thermometers at five-minute intervals, after they had become reasonably constant. Upon the basis of such observations calculation was easily made of the rate at which heat was *accumulating* in the bar at any given instant. In some cases this accumulation made a difference of several per cent in the amount of heat entering into the calculation of the conductivity. As an example of the method of observation, the following series made with the nickel bar will serve, the columns headed 1, 2, 3, etc., being readings of the thermometers no. 1, no. 2, no. 3, etc.: —

Time	1.	2.	3.	4.	5.	6.	7.	8.
	°	°	°	°	°	°	°	°
12:48	27.4	29.0	32.2	37.7	47.8	63.9	93.5	144.6
12:53	27.5	29.0	32.4	37.9	47.9	63.9	93.2	144.0
12:58	27.6	29.2	32.4	37.9	47.9	63.8	93.1	143.7
1:03	27.7	29.3	32.4	37.9	47.8	63.7	92.7	143.0

From these observations the following *estimate* may be made: —

Time	1.	2.	3.	4.	5.	6.	7.	8.
	°	°	°	°	°	°	°	°
12 : 50½	27.45	29.00	32.30	37.80	47.85	63.90	93.35	144.30
1 : 00½	27.65	29.25	32.40	37.90	47.85	63.75	92.90	143.35
Means	27.55	29.13	32.35	37.85	47.85	63.83	93.13	143.83
Rise in 10 minutes	.20	.25	.10	.10	.00	—.15	—.45	—.95

This was an unusually bad case.

Each bar was tested twice in a condition of approximate steady flow, that end which was heated in one test being the cool end in the other test. This trial of both ends in turn was probably suggested by the fact that the ends of the nickel bar were somewhat different in appearance, owing to that too rapid cooling of the molten metal which has already been mentioned.

For determining the rate of emission of heat each bar was twice heated and cooled as a whole. As only eight thermometers were available for this purpose, the middle hole was left unoccupied in all the rate-of-cooling experiments. The order of experiments was as follows: —

Cast Gun-Iron.	Southern Cast-Iron	Nickel.
May 30, rate of cooling.	May 31, rate of cooling.	June 10, rate of cooling.
June 2, steady flow.	June 2, steady flow.	" 11, steady flow.
" 7, rate of cooling.	" 4, rate of cooling.	" 11, " "
" 11, steady flow.	" 11, steady flow.	" 12, rate of cooling.

The bars were generally, if not in all cases, rubbed somewhat to brighten their surfaces just before being used. In experiments on the rate of cooling the whole length of the bar was first heated to about 115 or 120°, and as it cooled observations of all the thermometers upon it were made at regular intervals, — two-minute intervals at first and longer ones afterward, — until the bar was perhaps not more than 15° (in the earlier cases about 20° and in the later about 10°) above the general temperature of the room. The accordance of the two sets of cooling observations made with each bar was, on the whole, very satisfactory. From each set a curve was plotted. The following values taken from these curves will show how close the agreement was: —

Cast Gun-Iron.	Temp above that of Room.	Cooling per Second.
	°	°
May 30	30	.0098+
"	50	.0178+
"	80	.0300
June 7	30	.0102—
"	50	.0178—
"	80	.0300
Southern Cast-Iron.		
May 31	30	.0102—
"	50	.0178+
"	80	.0303—
June 4	30	.0100
"	50	.0182—
"	80	.0303+
Nickel.		
June 10	30	.0098—
"	50	.0178—
"	80	.0306—
June 12	30	.0100
"	50	.0178+
"	80	.0311—

In order that the air currents in the neighborhood of the bar during the cooling experiments might be, as nearly as practicable, like those prevailing during the steady flow observations, the Bunsen lamp within the tin protecting case already described was kept burning near one end of the cooling bar, the flame being of about the same height in all cases. A screen was placed between the box and the end of the bar to prevent direct radiation.

No attempt was made to represent by equations the temperature of the different parts of the bars during the condition of steady flow. The observations for every case were merely plotted carefully, with distances along the bars for abscissæ, and with temperatures, minus temperature of the room, for ordinates. Through the tops of the ordinates a smooth curve was drawn. The gradient of temperature at any point of the bar was found by measurement of the inclination of the curve at that point. The mean temperature of each division of the bar whose surface emission had to be considered was easily estimated from the mean height of the curve for that division. The amount of heat emitted from each such division was then estimated by reference to the curves, already mentioned, showing rate of cooling as a function of temperature of metal *minus* temperature of room. Wherever the specific heat of iron or of nickel appeared in the calculations, Naccari (*Atti della R. Accademia delle Scienze di Torino,* Vol. XXIII., 1887) was followed as an authority. He gives these values: —

	Sp. ht. of Iron.	Sp ht. of Nickel.
At 15° C.	0.1091	0.1057
At 50°	0.1113	0.1090
At 100°	0.1151	0.1137
At 150°	0.1196	0.1185

As any curve drawn, even when it runs smoothly and accurately through the points given by observation, may not represent the exact condition of things at intermediate points, and as there is liability to considerable error in determining the gradient of a line the curvature of which is everywhere changing, the conductivity was calculated for two points upon each curve of steady flow, both points lying between the two thermometers nearest the heated end of the bar. The difference between the two values thus found from any one curve is not to be explained by variation of conductivity with temperature. It is due, in the main, to errors of experiment or calculation. As there are two calculated values of conductivity from each curve of steady flow, and two such curves for each bar, there are four calculations of conductivity for each bar, but no two of these four are entirely independent, for the two sets of observations on the rate of cooling of each bar were combined for use with each curve of steady flow in that bar. The results are here presented: —

SOUTHERN CAST-IRON.

	Conductivity (c. g. s.).			Temperature.	
End no. 1 heated,	.1102	.1158	at	119° C.	112.5
June 2, 1890	.1214		"	106	
End no. 2 heated,	.0987	.0981	"	123	116.5
June 11, 1890	.0975		"	110	
Mean		.107			114

CAST GUN-IRON.

	Conductivity (c. g. s.).			Temperature.	
End no. 1 heated,	.1049	.1045	at	116° C.	110.5
June 2, 1890	.1042		"	105	
End no. 2 heated,	.1011	.1036	"	121	115.0
June 11, 1890	.1062		"	109	
Mean		.104			113

IMPURE CAST NICKEL.

	Conductivity (c. g. s.)			Temperature.	
End no. 1 heated,	.108	.1065	at	127° C.	116
June 11, 1890	.105		"	115	
End no. 2 heated,	.1030	.1062	"	128	117
June 11, 1890	.1095		"	116	
Mean		.106			116

The avowedly rough and hasty character of the experiments being considered, the agreement of the results obtained in the case of gun-iron and in the case of nickel is entirely satisfactory. In the case of the other bar, the results do not agree among themselves so well as one could wish, although, in view of the acknowledged difficulty which attends experiments upon thermal conductivity, they should not be considered surprisingly discordant. I can offer no explanation of the fact that both the largest and the smallest calculated values of the conductivity were obtained from this bar. The mean value, it will be observed, is not very far from the mean obtained with the gun-iron bar. The mean value for each of the iron bars is, I believe, smaller than any other investigator has recorded for iron, though not smaller than has been found for Bessemer steel.

The following values are taken from Landolt and Börnstein's *Physikalisch-Chemische Tabellen :* —

	Temperature.	Conductivity.	Observer.
Iron	100° C.	.1417	Angström.
"	0	.1988	"
"	100	.1627	Lorenz.
"	0	.1665	"
Wrought-Iron	100	.1567	Forbes.
" "	0	.2070	"
Bessemer Steel	15	.0964	Kirchhoff and Hansemann.

According to Kirchhoff and Hansemann (*Wied. Annalen,* Vol. IX. p. 5), the conductivity of iron (in c. g. s. units) is expressed by the formula $.1694 - .00034\ (t - 15)$.

This gives for 15° C. the value .1694,
and for 100° C. the value .1405.

The iron used by Lorenz had the density 7.828 (*Wied. Annalen,* Vol. XIII. p. 438), and was therefore not cast-iron. That used by

Kirchhoff and Hansemann (*Wied. Annalen*, Vol. IX. p. 6) contained only 0.129 per cent of carbon, and was therefore not cast-iron. I have as yet found no description of the iron used by Angström, but it is probable that he too used a tolerably pure specimen. Reviewing the course of my experiments, I find no reason for supposing my values to be, as a whole, much too low. The very great interval of temperature, about 50°, between thermometers 8 and 7, next the heated end of the bars, was no doubt too great for the greatest precision of results, but a number of calculations of the conductivity for points between thermometers 7 and 6 give a mean very near those found for points between 8 and 7. The natural conclusion is, that cast-iron has a much smaller conductivity than wrought-iron.

But whatever may be the value of my results as to iron alone, there can be little doubt that the main object for which the experiments were made, namely, to determine approximately the relative conductivity of cast iron and cast nickel, has been attained. The thermal conductivity of the nickel here used is very nearly the same as that of the cast-iron bars with which it was compared.

In spite of the very considerable amount of laborious study that has been devoted to the thermal conductivity of iron, authorities differ widely in their conclusions, especially upon this particular, the change of conductivity with change of temperature, as the numbers above given show. This difference comes in part from different opinions as to the change of specific heat of iron with change of temperature. The work of a number of investigators within the past ten years has added greatly to our knowledge upon this latter subject, and possibly recalculations of thermal conductivity from old observations might now be made with advantage.

I hope soon to make trial of a method for estimating thermal conductivity somewhat different from any heretofore used.

January 7, 1893.

I have recently, with the help of students, made additional observations upon steady flow and the rate of cooling in the Southern cast-iron bar, placed now in the main lecture-room of the Physical Laboratory. The new observations on rate of cooling extended about 46° only, — from +110° to +64°; but for this range they indicated a rate about 10% greater than was found in the basement in 1890. A rough calculation from this new study of the bar indicates for end no. 1 a conductivity practically the same as that found for this end before; but for end no. 2, a conductivity about 6% greater than previous observations showed.

Chemical analysis of borings from the nickel bar showed the following composition: —

Nickel	85.44%
Iron	7.56
Silicon	0.42

with small quantities of antimony, arsenic, copper, manganese, phosphorus, sulphur, and tin.

Analysis of borings from the gun-iron bar showed: —

Carbon (total)	3.64%
Phosphorus	0.59
Silicon	1.33

XX.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXIX. — ON SOME EXPERIMENTS WITH THE PHONOGRAPH, RELATING TO THE VOWEL THEORY OF HELMHOLTZ.

By Charles R. Cross and George V. Wendell.

Presented May 24, 1892.

The value of the phonograph as an aid in the study of the theory of vowel tones was recognized almost immediately upon the invention of that instrument, and it was employed for this purpose as early as 1878 by Messrs. Jenkin and Ewing,* and also by Dr. C. J. Blake in connection with one of the present writers. The experiments of the last mentioned observers were designed to aid in the solution of the question whether it is a fact, as assumed by Helmholtz, that each vowel possesses a distinctive character due to the presence of a particular tone or tones, which are the resonance notes of the mouth cavity when shaped for the utterance of the corresponding vowel. The method employed, and the results obtained were described in a letter to *Nature* (Vol. XVIII. p. 93), so that a brief reference to them will suffice.

The plan followed was to speak a vowel into the mouthpiece of the phonograph when the cylinder was revolved at a certain rate, and then to reproduce the tone with a varying rate of revolution, both faster and slower than that used when the record was impressed upon the cylinder. Any particular resonance note, if present, would then have its pitch raised or lowered, and presumably the vowel sound would be correspondingly altered.

This was found to be the case, the vowel apparently changing with change of speed of the cylinder. For example, the vowel ō changed to *e* on increasing the speed to a rate considerably above that at which the former vowel was impressed upon the recording cylinder, and fell to *â* when the speed of the cylinder was carried considerably below that at which the record was made.* Various other results of the same character were secured.

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* See Nature, Vol. XVII. p. 384; Trans. Roy. Soc. Edinburgh, Vol. XXVIII. p. 745.

The accuracy of these results was questioned, but they were shortly afterwards confirmed by A. G. Bell and F. Blake,† and others. The only form of phonograph in existence at that time, however, remarkable as it then seemed to be, was extremely crude and imperfect, the tin-foil employed as a medium for receiving the record not being well fitted to receive and retain the delicate impressions of the sounds of the human voice. Upon the commercial introduction of the modern phonograph of Edison, in which a cylinder of wax replaces the tin-foil, and which leaves little to be desired so far as clearness of articulation is concerned, it appeared to be desirable to repeat the early investigations just referred to, with the improved instrument. After our work was well advanced, our attention was called to investigations in the same direction by Hermann.‡ But his very valuable researches on vowel tones, and their study by the aid of the phonograph, have mostly employed methods other than the one under consideration, and only some general results by this particular method seem to have been published by him. These are in accordance with the observations described in the letter to *Nature* already mentioned.

The method followed in the present series of experiments is identical with that used in the earlier studies referred to. As the cylinder of the modern phonograph is rotated by an electro-motor furnished with a good speed-governor, it was easy to vary the speed within moderately wide limits, and to keep it at a tolerably definite and known rate, which was done in most of our experiments. In some of these, however, only general results were sought for, and no attempt was made to measure the speed.

We proceed to give a detailed description of a few of our more general preliminary experiments, which is followed by a statement in tabular form of the later and more precise observations. In the former, we have noted only those sounds which seemed most prominent in the different series.

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* In this paper the sounds of the different vowels are denoted by the conventional signs employed in the Century Dictionary. Certain other signs used are explained later.

† See American Journal of Otology, Vol. I. p. 163.

‡ Cent. f. Physiologie, 1890, Vol. IV. p. 242; Pflüger's Archiv, 1890, Vol. LXXIV. p. 42.

(1) The vowel *ö* was spoken into the speaking-tube of the phonograph when the cylinder was rotated at the lowest speed at which it was possible to drive it with the governor used, — about one half-revolution per second. The vowel was then reproduced with a gradually increasing speed of the cylinder up to the highest possible speed, — about three and one half revolutions per second. The experiment was repeated several times, and with different observers. The sounds heard as represented were

ö ō ou ü a.

(2) The vowel *ö* was spoken into the mouthpiece at a speed of about one revolution per second. On reproducing it at lower rates down to about one half-revolution per second, the vowel sound was still heard as *ö*, but becoming more and more guttural, until at the lowest speed it sounded like a deep gurgle.

(3) The vowel *ō* spoken with a moderately low speed of the cylinder, and reproduced with gradually increased speeds from the lowest possible to the highest, gave the following sounds: —

ö ō ọ̄ ou ä a.

(4) The vowel *ō* was spoken into the instrument at the highest attainable speed, and repeated a number of times, the speed of the cylinder meanwhile being lowered gradually, so that the vowel in question was impressed upon the cylinder at a variety of speeds, from the highest to the lowest. It was then reproduced with gradually increasing speed of the cylinder, beginning with the lowest possible. This procedure was well adapted to give a large number of vowel sounds in succession. The reproduced vowels noted were

ö ō ō ou ä a i.

(5) The vowel *ō* spoken at the lowest possible rate was reproduced at gradually increasing speeds. The sounds heard were

ō ä a e i.

(6) The vowel *ō* spoken at a rate of about one revolution per second was reproduced at a lower speed as *ö* and at the lowest attainable speed as a very deep guttural *ö*.

(7) The vowel *ē* spoken with a cylinder speed of about one revo-

lution per second. and reproduced at speeds varying from the lowest to the highest attainable, gave the following sounds:—

ü ē ẹ̄ i.

The last mentioned sound was given out only at the extreme upper limit of speed.

(8) The vowel *ē* spoken with a speed of about two revolutions per second was reproduced at a lower speed as *ü*, but at all attainable higher speeds still retained its vowel character as *ē*.

The following tables contain the results of later experiments in which the speed of revolution was measured. Table I. contains results reached when a single vowel was sounded and reproduced at various speeds. The first column contains the serial number of the experiment; the second, the name of the vowel; the third, the rate of revolution of the cylinder of the phonograph when the vowel was spoken into the mouthpiece and its record impressed upon the wax; and the fourth, the vowel sounds observed when the spoken sound was reproduced at various speeds, R_1. The speed is denoted in revolutions per second.

TABLE I.

No.	Vowel Spoken.	R	Vowels reproduced.					
1	*ō*	1	R_1	½	1	2	3	
			Vowel reproduced .	*ö*	*ō*	*ou*	*ou*♯ (almost *ä*♯).	
2	*ō*	1	R_1	½	1	2	3	
			Vowel reproduced .	*ö*	*ō*	*ou*	*ou*♯ (less sharp than in 1).	
3	*ō*	2	R_1	1	2	3	3½	
			Vowel reproduced .	*ö*	*ō*	*ọ̄*	*ou*	
4	*ä*	1	R_1	½	1	3		
			Vowel reproduced .	*ô*	*ä*	*a*		
5	*ä*	3	R_1	3	2	1	½	
			Vowel reproduced .	*ä*	*ô*	*ō*	*ö*	
6	*ä*	2	R_1	½	1	2	3	
			Vowel reproduced .	*ö*	*ô*	*ä*	*a*	
7	*ā*	½	R_1	½	1	2	2½	3
			Vowel reproduced .	*ā*	*ä*	*a*	*e*	*ị*
8	*i*	1	R_1	½	1	2		
			Vowel reproduced .	*e*		*i*		

TABLE II.

No.	Vowel Spoken.	*R*	Vowels reproduced.				
9	*ö ō*	1	*R*₁	1	2		
			Vowel reproduced .	*ö ō*	*ō ou*		
10	*ō ö*	1	*R*₁	1	2		
			Vowel reproduced .	*ō ö*	*ou ō*		
11	*ē ē ō*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ē e ō*	*ē ē ou*	*ẹ̄ ẹ̄ ä*	
12	*ē ō ē*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ē ō ē*	*ē ou ē*	*ẹ̄ ou♯ ẹ̄*	
13	*ē ö ē*	1	*R*₁	1	2	3	3½
			Vowel reproduced .	*ē ö ē*	*ē ō ē*	*ẹ̄ a ẹ̄*	*ẹ̄ a♯ ē*
14	*ō ē ē*	1	*R*₁	1	1½	2	
			Vowel reproduced .	*ō ē ē*	*ou ē ē*	*ou♯ ẹ̄ ẹ̄*	
15	*ō ö ā*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ō ö ā*	*ou ō a*	*ou♯ â e*	
16	*ö ō ā*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ö ō ā*	*ō ou a*	*ọ̄ ä e*	
17	*ā ö ō*	1	*R*₁	1	2	3	
			Vowel reproduced .	*á ö ō*	*a ō ou*	*a♯ ọ̄ ou♯*	
18	*ō ē ā ī ö*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ō ē ā ī ö*	*ou ẹ̄ ā♯ ị♯ ō*	*ou♯ ẹ̄ ị̄ a♯ ō*	
19	*ō a ī ö ē*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ō a ī ö ē*	*ou a♯ ị ō ẹ̄*	*ou♯ a♯ ī♯ ō ē*	
20	*ö ō ä e i*	1	*R*₁	1	2	3	
			Vowel reproduced .	*ö ō ä e i*	*ō ou a♯ ẹ ị*	*ọ̄ ou♯ a♯ ị u♯*	

In addition to what has already been said as to the conventional signs used by us to indicate the different vowel sounds, it should be stated that in the preceding tables and subsequent pages a ♯ following a vowel indicates a rise in its characteristic note, generally with an accompanying nasal quality. Thus in (1), (2), (12), and elsewhere, the sound denoted by *ou♯* is nasal. In (1) it approaches a nasal *ä*. In (13) and elsewhere, the sound denoted by *a♯* lies between *a* and *e*, and closely approaches or even passes into the French nasal *in*. The sound *ā♯* in (18) approaches *ī*. The sound *ī♯* in (18) is strongly nasal in quality. The *u♯* in (20), however, is not at all nasal, but is a very high *u* with a resonance note much higher than that of *ị̄*.

Several series of experiments were also tried in which a number of vowel sounds in succession were impressed upon the cylinder, and subsequently reproduced at different speeds, — a method which enables one to compare more readily the changes in the various vowels with one another. The results of these comparisons are found in Table II.

A careful comparison of the various changes indicated in the preceding tables will show a close accordance between the results of different experiments. But there will be noticed a few apparent discrepancies. Thus in (15) *ō* rises to *ou*♯ and in (16) to *ä*; in (15) *ö* rises to *â*, and in (16) to *ọ̄*, while *ā* rises to *e* in both series. These and such other like results as exist are due chiefly to the fact that it was difficult to measure the speed with any great exactness at the higher rates, or to maintain this speed absolutely uniform, and a slight increase in speed would suffice to change the results as stated in (15) to those of (16). The vowel *ā* sustains the same change in each, notwithstanding this difference in speed, because the *e* into which it changes is more persistent than the other vowels in the series, as will be more fully explained a little later. It will also be instructive to compare (16) with (17). The *ā* in the former rises to *e* on passing from one to three revolutions, while in the latter it rises only to *a*♯, which sound would have passed into *e* on a slight increase of speed. In (16) the speed was doubtless a trifle higher than in (17) as well as in (15).

It must also be remembered that at certain stages a sound will be on the point of passing from one recognized vowel into another, so that it may be difficult to denote its sound exactly by any of the conventional signs usually employed. For this reason it might be preferable to substitute the symbols used by Mr. Melville Bell in his "Visible Speech."

Furthermore, we have noticed in some cases that a very trifling difference in the quality of the vowel impressed upon the cylinder at a low speed may cause a decided change in the vowel sound given out at a considerably higher speed. Thus, the vowel *e* reproduced at increased speeds passes into a high *ị̄* and then into ***i***. But if a series of *e*'s be spoken into the instrument, it is possible to find a speed of reproduction such that some of them are heard as *ị̄*'s and some as *i*'s. On raising the speed the *ị̄*'s tend to rise to *i*, and on lowering it the *i*'s tend to fall to *ị̄*.

Some interesting peculiarities of different vowels were observed in the course of our experiments.

It was noticed that, in several cases where the vowel seemed to have quite lost its peculiar quality, there was nevertheless a certain reminiscence, so to speak, of its original character remaining. This appeared to be due to the logographic differences among the various vowels. Of course, the logographic characteristics of any vowel are not altered by the speed at which the sound is reproduced, so that in many cases we necessarily reproduce a sound with a characteristic resonance note belonging to one vowel and a logographic character belonging to another. Where the logographic character is clearly marked, this may enable one to recognize the vowel sound originally spoken into the phonograph, even though the characteristic resonance note is quite changed. This is especially true when the vowel forms part of a word.

There also appears to be a great difference among different vowels in what we may call the persistence of their vowel character when the speed of reproduction is varied. Whereas some, as *ö*, *ō*, and *ä*, change their character completely on increasing the speed, say to double its original rate, others change far less. The vowel *ē* seems particularly persistent under a large change in speed. With it as with all vowels there is necessarily a shortening at higher speeds, as denoted in the tables by a dot placed under the letter; but apart from this the speed may be varied more than for any other vowel studied by us before any marked change in its quality appears.

In order to form some estimate of the extent to which the context would influence the judgment as to the character of a vowel sound, the experiment was tried of reproducing at different speeds a sentence or verse spoken into the instrument. Thus the words from a negro melody containing the vowel *ō* many times repeated were spoken, as follows: —

"Roll, Jordan, roll!
Roll, Jordan, roll!
I want to go to heaven when I die
To hear old Jordan roll."

These words were impressed upon the cylinder at a speed of three revolutions per second, and were reproduced at speeds of two revolutions and one revolution per second respectively, with the following results. At two revolutions the *ō*'s were in all cases plainly recognizable though lengthened; but at one revolution the quality was completely altered, *ō* having become changed to *ö* in all cases. Like results were observed in other sentences containing the vowel *ō*.

In like manner the sentence "This was the noblest Roman of them all" was impressed upon the cylinder at a speed of one revolution. Reproduced at two revolutions, the ō's had a sound which closely approached *u*. Lowering the speed slightly changed it to a very short ọ̄ ; and raising the speed slightly, to a clear *u*. At three revolutions the quality of all the vowels was so completely changed that the sentence was entirely unintelligible even to one knowing what it really was, the rapidity of the speech, as reproduced, however, contributing largely to this lack of intelligibility. To avoid this latter source of difficulty, the same sentence was spoken into the instrument at a speed of two revolutions, and reproduced at one revolution and also at three revolutions. At the lower speed the *i* in "this" changed to *a*, so that, the *s* in "this" being rather indistinct, the word seemed almost to have changed to "that." But the ō's, while deepened in quality, did not apparently actually change to ö. Lowering the speed still more caused a closer approach to this, but the ō quality still seemed to persist. This was doubtless due in part to the association of the sound with the word, and in part to the acoustic effects due to logographic pressure, and to the connection of the vowel with the preceding consonants. To study these, the same sentence, preceded by four ō's and followed by the same number, was spoken at two revolutions and reproduced at one revolution. The separate ō's seemed to fall to ö, and there was likewise a perceptible fall in the same sounds in the body of the sentence, but these seemed still to retain their ō sound. To test the matter still further, the same sentence with the ō's mispronounced was spoken into the phonograph, at a speed of one revolution, as follows: "This was the nöblest Röman of them all." On reproducing it at two revolutions the ö's changed to ō, and the sentence was clearly heard with the mispronounced words rectified, and as distinct as if they had been properly pronounced when impressed upon the cylinder, and reproduced with the same speed of the cylinder as when uttered. Lowering the speed below one revolution, the ö sounds became still deeper and clearer.

As the vowels ō and ö are more persistent in their character than some others, a similar experiment to those already described was tried with the line, "Though the harbor bar be moaning." This was impressed upon the cylinder at a speed of one revolution per second. Reproduced at two revolutions, the words "härbor bär" became "harbor bar" (*a* as in *hat*), and at three revolutions the ä's in the same words assumed a nasal quality somewhat approaching the French nasal *in*.

The further experiment was performed of sounding the five vowels *ā ē ī ō ū* successively into the cylinder when this made one revolution per second, and reproducing them at three revolutions. It was found that the quality of the different vowels was altered so that they were unrecognizable by one ignorant of the sounds which had actually been spoken by the voice. The same result was reached with the vowels *ä e ē ọ̄ ö*, and also with *ö ō ä e i*. The last mentioned series, which is No. 20 in the tables, was impressed upon the cylinder at a speed of one revolution, and reproduced at two and at three revolutions, approximately. At two revolutions the series seemed to have changed to *ō ou a♯ ẹ ị*, the *a♯* closely approaching the French nasal *in*. At three revolutions the sounds heard were *ọ̄ ou♯ a♯ ị̄ u♯*, the *a♯* being a clear nasal *in* and the *u♯* a very short *u* with a high resonance note.

The limitations in speed of the phonograph cylinder, as the instrument is constructed for practical purposes, have thus far prevented us from carrying the range of changes in the pitch of the reproduced sounds as far as is desirable. This defect we purpose to remedy by suitable modifications in the driving gear of the apparatus. For reasons already explained, it is also desirable to measure the relative rates of rotation more accurately than we have been able to do with the commercial form of the phonograph.

We hope that we may be able to continue this investigation by a more systematic study of the behavior of the reproduced vowel sounds, and likewise to consider the effect of changed pitch in reproduction upon the various consonantal sounds.

In connection with the present subject, it is interesting to consider the unconscious testimony to the existence of different characteristic resonance notes for the different vowels which is given by various onomatopoetic words. The words used to denote various sounds form an excellent example, as will appear from the following list of a few such words in which the pitch of the sound denoted is higher as the list proceeds: — boom, gurgle, roll, toll, roar, slump, thump, crash, smash, crack, snap, bang, jingle, ring, hiss. It will be observed that the vowels in the later words are those with higher resonance notes.

Rogers Laboratory of Physics,
May, 1892.

XXI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROMTRINITROBENZOL.*

SECOND PAPER.

By C. Loring Jackson and W. H. Warren.

Presented June 15, 1892.

In our first paper on this subject we described some experiments which led to the replacement of nitro groups in symmetrical tribromtrinitrobenzol by ethoxy or methoxy radicals. These observations seemed to us of special interest because the three nitro groups are in the meta position in this compound, and, so far as we were aware, no case was known in which a nitro group in this position to others had been removed from the benzol ring. In fact the so-called rule of Laubenheimer stated that a nitro group is replaced only when it is in the ortho position to another. Even with the halogens cases where a radical in the meta position exercises a loosening effect on another are very rare, the only one which occurs to us being the conversion of symmetrical tribrombenzol into dibromanisol by the action of sodic methylate.†

Soon after the appearance of our paper C. A. Lobry de Bruyn published an account ‡ of some experiments with symmetrical trinitrobenzol and sodic methylate from which he obtained dinitroanisol, thus again removing a nitro group in the meta position to others. At the same time in an interesting discussion § of the replacement of nitro groups in aromatic compounds he showed that Laubenheimer's rule must be abandoned, since para as well as ortho nitro

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[*] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

[†] Blau, Monatsh. f. Ch., VII. 630.

[‡] Rec. Trav. Ch. des Pays-Bas, IX. 208.

[§] Ibid., IX. 210.

compounds are attacked by alcoholates and other reagents with the removal of nitro groups. This publication brought to our notice an earlier paper* by him, in which he states that by the action of alcoholic potassic cyanide on metadinitrobenzol one nitro group is replaced by the ethoxy (or methoxy) radical, but at the same time an atom of cyanogen is substituted for one atom of hydrogen, giving as the product $C_6H_3NO_2OC_2H_5CN$. This curious result seems to have more affinity with the additions of hydrocyanic acid to nitrohalogen benzols studied by v. Richter † than to simple substitution; but nevertheless we have here the replacement of a meta nitro group by another radical. As Lobry de Bruyn's later work was published almost simultaneously with ours (although a little later), and had grown out of his earlier researches, we felt that the study of substitutions of nitro groups in simple trinitro compounds should properly belong to him, and after a pleasant correspondence on the subject it has been agreed that he should follow out this line of work, while we confine ourselves, so far as the removal of nitro groups is concerned, to the completion of our study of tribromtrinitrobenzol.

At present, therefore, we know only three meta nitro compounds from which nitro groups have been removed, dinitrobenzol, symmetrical trinitrobenzol, and symmetrical tribromtrinitrobenzol.

Lobry de Bruyn's work shows that the removal of nitro groups observed by us is caused by the position of these nitro groups, but the presence of the three meta bromine atoms evidently also has a loosening effect on the nitro groups, as we have replaced two of these groups by ethoxy radicals, whereas in the trinitrobenzol only one was replaced.

In taking up the study of the subject again, we first examined the action of tribromtrinitrobenzol and sodic ethylate more carefully, to see whether the bromine atoms were not also affected by it, and found that in addition to the tribromnitroresorcine diethylether there is always formed a quantity of trinitrophloroglucine triethylether, $C_6(OC_2H_5)_3(NO_2)_3$, melting at 119–120°; as however this substance is easily decomposed by sodic hydrate, the amount of it obtained as such is small, unless special precautions are taken to exclude atmospheric moisture. When such precautions are not taken, the trinitrophloroglucine triethylether is converted into the diethylether $C_6OH(OC_2H_5)_2(NO_2)_3$, melting at 89°, or trinitrophloroglucine itself, $C_6(OH)_3(NO_2)_3$, (which melts at 167° instead of 158°, the point given by Benedikt,*) and these substances pass into the aqueous wash-waters as sodium salts. It follows therefore that the action of sodic ethylate on tribromtrinitrobenzol consists of the two following reactions, which take place parallel to each other: —

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* Rec. Trav. Ch., II. 205.

† Ber. d. ch. Ges., IV. 465, VII. 1145, VIII. 1418.

$$C_6Br_3(NO_2)_3 + 3\,NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3\,NaBr.$$
$$C_6Br_3(NO_2)_3 + 2\,NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2\,NaNO_2.$$

We observed further, that, if benzol and alcohol were used as the solvents instead of alcohol alone, more of the phloroglucine ether was obtained than when the solvent was only alcohol, and this led us to study the action quantitatively by determining the amounts of sodic nitrite and bromide formed, when we found that the amount of nitrite averaged with the benzol and alcohol 33.49 per cent; with alcohol alone, 45.92 per cent. There was also a difference in the reverse direction with the sodic bromide, but the percentages of this obtained under parallel conditions varied so materially that no careful comparison was possible. The percentages of sodic nitrite removed were, on the other hand, remarkably constant. We have not succeeded in finding any satisfactory explanation for this effect of the presence of benzol in promoting the formation of the trinitrophloroglucine triethylether (produced by the first reaction), and diminishing the amount of tribromnitroresorcine diethylether formed by the second reaction given above.

We have also tried the action of several other alcoholates on tribromtrinitrobenzol, obtaining the following compounds: — $C_6Br_3NO_2(OCH_3)_2$, melting at 126°; $C_6(OCH_3)_2OH(NO_2)_3$, melting at 77–78°; $C_6(OC_3H_7)_3(NO_2)_3$, from normal propyl alcohol, melting point 109–110°; the corresponding isocompound melting at 130°; and $C_6(OCH_2C_6H_5)_3(NO_2)_3$, melting at 171°. A quantitative comparison of the amounts of sodic nitrite formed by different alcoholates indicated that the percentage removed diminishes as the molecular weight of the alcohol increases, but there were several exceptions to this general rule.

We have also found that sodic ethylate decomposes the triphenylether of trinitrophloroglucine, converting it into the triethylether, while phenol is set free; and that sodic ethylate when heated with the tribromnitroresorcine diethylether removes from it two atoms of bromine which are replaced by hydrogen, so that the product is bromnitroresorcine diethylether, $C_6H_2BrNO_2(OC_2H_5)_2$, melting at 115°; — an observation which will be of value in discovering the cause of the strange replacements of bromine by hydrogen so often found in the course of this work.

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* Ber. d. ch. Ges., XI. 1376.

PART I.

ACTION OF SODIC ETHYLATE ON TRIBROMTRINITROBENZOL.

IN our earlier paper * on this subject we showed that sodic ethylate brought about a replacement of two of the nitro groups in tribromtrinitrobenzol by two ethoxy radicals forming tribromnitroresorcine diethylether, $C_6Br_3NO_2(OC_2H_5)_2$, as the principal product if alcohol was used as the only solvent and the mixture carefully cooled. There remained, however, several points which needed more careful examination, especially the effect upon the reaction of differences of temperature, the effect of using different solvents, and the source of the sodic bromide which was always formed in addition to the sodic nitrite. The results of our work on these subjects are given in the following paragraphs.

The experiments described in our first paper had led us to think that the tribromnitroresorcine diethylether was formed only when the mixture of tribromtrinitrobenzol and sodic ethylate was carefully cooled. To test the accuracy of this conclusion, we dissolved some tribromtrinitrobenzol in alcohol and a little benzol with the aid of heat, and added to the boiling solution in small quantities at a time enough sodic ethylate to give three molecules of the ethylate to each molecule of tribromtrinitrobenzol. As soon as all the ethylate had been added, the bright scarlet solution was allowed to cool, and then evaporated spontaneously. The aqueous washings of the residue gave a strong test for a nitrite, and also for a bromide. The portion insoluble in water was purified by crystallization from alcohol until it showed a melting point of 100° (the tribromnitroresorcine diethylether melts at 101°), when it was analyzed with the following result: —

0.2076 gr. of the substance gave by the method of Carius 0.2601 gr. of argentic bromide.

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* These Proceedings, XXV. 183.

	Calculated for $C_6Br_3NO_2(OC_2H_5)_2$.	Found.
Bromine	53.57	53.32

This analysis with the melting point leaves no doubt that the substance is the expected tribromnitroresorcine diethylether, and therefore that the temperature of the reaction does not affect the nature of the principal product. We have accordingly omitted the cooling in our subsequent preparations of this body, simply allowing the mixture of tribromtrinitrobenzol, sodic ethylate, and alcohol to stand over night at ordinary temperatures.

The Modification of the Action when Benzol is used as one of the Solvents.

To study this subject the following experiment was tried. 10 gr. of tribromtrinitrobenzol were dissolved in dry benzol and an alcoholic solution of the sodic ethylate from 1.5 gr. of sodium added (these proportions are essentially three atoms of sodium to each molecule of tribromtrinitrobenzol). The first drop of the solution of sodic ethylate turned red as it was added, the color fading to yellow as the drop mixed with the liquid, so that, after all the ethylate had been added, the liquid had assumed an orange-red color. No evolution of heat was observed during the reaction. To make sure that the action was complete, the mixture was allowed to stand over night in a corked flask at ordinary temperatures, and then allowed to evaporate spontaneously, after which the residue was washed with water to remove the soluble salts.

Substances insoluble in Water. — The residue after washing with water was crystallized repeatedly from alcohol, and in this way a considerable quantity of the tribromnitroresorcine diethylether melting at 101° was obtained from the first crystals, while the mother liquors yielded a smaller quantity of another substance which when pure melted at 119–120°. This was dried at 100°, and analyzed with the following results: —

I. 0.2159 gr. of the substance gave on combustion 0.3284 gr. of carbonic dioxide and 0.0914 gr. of water.

II. 0.2080 gr. of the substance gave 22.5 c.c. of nitrogen at a temperature of 21°, and a pressure of 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found. I.	Found. II.
Carbon	41.75	41.49	
Hydrogen	4.35	4.70	
Nitrogen	12.17		12.30

It contained no bromine. There can be no doubt, therefore, that the product was the triethylether of trinitrophloroglucine, and that the formation of this substance produced the sodic bromide which was always obtained by the action of sodic ethylate on tribromtrinitrobenzol.

Properties of Trinitrophloroglucine Triethylether. — This substance crystallizes in long slender plates, terminated usually by one plane at a very sharp angle to the sides. These crystals are often united longitudinally into broader plates, which frequently have serrated ends, and may reach more than a centimeter in length and a millimeter in breadth. The color is white, but it turns brownish on exposure to the air. It melts at 119–120°; is soluble in cold ethyl or methyl alcohol, freely soluble in either of these solvents when hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroine; essentially insoluble in water, whether cold or hot. The three strong acids have no perceptible action on it hot or cold, except that it is dissolved by hot strong nitric acid, but on dilution it is precipitated unchanged, to judge by the melting point. We have tried no experiments on its saponification by the long continued action of acids. A cold aqueous solution of sodic hydrate had no action upon it, and only a slight action when heated, but in alcoholic solution sodic hydrate decomposes it even in the cold, more rapidly when hot, forming a reddish yellow solution of the sodium salt of a phenol.

In addition to the tribromnitroresorcine diethylether and trinitrophloroglucine triethylether, we have always obtained from the crystallization a considerable amount of a substance which accumulated in the mother liquors and separated from its alcoholic solution as an oil solidifying after standing for some weeks. We have devoted a great deal of time to the study of this substance, because it appeared in such quantity that we thought it must be a principal product of our reaction; but this work has shown that it consists principally of the products already described, mixed with very little of an oily substance which prevents them from crystallizing as usual. In a preparation from 30 gr. of tribromtrinitrobenzol, the mother liquors gave 4.3 gr. of the more or less liquid fraction, but this amount was reduced to 1.2 gr. after removing the trinitrophloroglucine triethylether completely by treatment with alcoholic sodic hydrate, and the tribromnitroresorcine diethylether as nearly as possible by crystallization from alcohol of the mixture solidified by standing for several months. All our attempts to free the oily product completely from the tribromnitroresorcine diethylether have failed, so that we are unable to give any account of its composition.

Products soluble in Water. — In purifying the products of the action of sodic ethylate upon tribromtrinitrobenzol, the aqueous solution formed by washing the residue from spontaneous evaporation contained a large amount of organic matter, as was indicated by its orange-red color. In order to determine its nature, the solution was acidified with dilute sulphuric acid, which gave a precipitate, but did not remove all the organic matter present, since the filtrate still showed a strong yellow color. This precipitate was washed with water, in which it is nearly insoluble, until the washings ceased to show a yellow color, and then purified by converting it into its sodium salt, filtering the solution, reprecipitating with dilute sulphuric acid, and finally crystallizing from dilute alcohol until it showed the constant melting point 89°, when it was dried *in vacuo* and analyzed with the following results: —

0.2285 gr. of the substance gave on combustion 0.3145 gr. of carbonic dioxide and 0.0817 gr. of water.

	Calculated for $C_6(OC_2H_5)_2OH(NO_2)_3$.	Found.
Carbon	37.85	37.53
Hydrogen	3.47	3.97

To confirm these results, a portion of the substance was treated with an aqueous solution of less than the calculated amount of sodic hydrate necessary to convert it into the sodium salt, the solution of the salt was filtered from the unaltered phenol, the filtrate evaporated to dryness, and the residue washed with benzol to remove any traces of the free phenol which might have dissolved in the water. It was then dried at 100°, and the sodium salt thus obtained analyzed with the following results: —

I. 0.1498 gr. of the substance yielded 0.0329 gr. of sodic sulphate.

II. 0.2410 gr. of the salt gave 0.0524 gr. of sodic sulphate.

	Calculated for $C_6(OC_2H_5)_2ONa(NO_2)_3$.	Found.	
		I.	II.
Sodium	6.78	7.11	7.04

These analyses leave no doubt that the substance is the diethylether of trinitrophloroglucine. As it has not been described heretofore, we add its properties.

Properties of the Diethylether of Trinitrophloroglucine. — This substance crystallizes in square-ended rather short prisms, or in longer flat needles, also usually with square ends, although sometimes instead of this they are very sharp; both forms are frequently arranged in fan-like groups. It has a straw-yellow color, and melts at 89°. Very freely soluble in ethyl or methyl alcohol, ether, benzol, glacial acetic acid, chloroform, or acetone; soluble in carbonic disulphide; very slightly soluble in ligroine; slightly soluble in cold water, more soluble in hot; dilute alcohol is the best solvent for it. The three strong acids have no apparent action on it, hot or cold. Sodic hydrate dissolves it, forming an orange-red sodium salt, which crystallizes in fine needles. Ammonic hydrate dissolves it rather slowly, forming a yellow solution. Solutions of sodic or acid sodic carbonate also dissolve it with evolution of carbonic dioxide forming yellow solutions; it is evident, therefore, that the substance possesses strongly acid properties.

The filtrate from the diethylether of trinitrophloroglucine, which had changed from red to yellow on acidification, after concentration on the water bath deposited upon cooling rather ragged thick yellow needles; but if the evaporation was carried on spontaneously, yellow hexagonal prisms were obtained, which dissolved in alkalies more easily than in water, and gave, according to the amount of alkali used, red or yellow salts, crystallizing in hair-like needles, properties which indicated that the substance was a polyatomic nitrophenol, probably the trinitrophloroglucine. This substance has been described by Benedikt * as crystallizing from water in hexagonal prisms, and melting at 158°; we accordingly purified our substance by crystallization from water, but found that it melted as high as 167°. In spite of the want of agreement between this melting point and that given by Benedikt, the crystalline form and other properties indicated that the substance was trinitrophloroglucine, and this was proved to be the case by the following analyses. As Benedikt found that trinitrophloroglucine contains one molecule of water of crystallization, we examined our substance for this.

I. 0.7721 gr. of the air-dried substance when heated to a temperature of 105° lost 0.0477 gr.

	Calculated for $C_6(OH)_3(NO_2)_3H_2O$.	Found. I.
Water	6.45	6.18

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* Ber d. ch. Ges., XI. 1376.

The air-dried substance lost 0.0015 gr. at 56°, and showed a tendency to sublime at 105°.

II. 0.2126 gr. of the compound dried at 105° gave on combustion 0.2105 gr. of carbonic dioxide and 0.0304 gr. of water.

III. 0.2260 gr. of the compound dried at 105° gave 31.2 c.c. of nitrogen at a temperature of 17° and a pressure of 775.8 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$.	Found.	
		II.	III.
Carbon	27.58	27.01*	
Hydrogen	1.15	1.59	
Nitrogen	16.69		16.37

It is evident from these analyses that the substance is *trinitrophloroglucine*, and therefore it becomes important to explain the very marked difference between the melting points observed by Benedikt and by us. We are inclined to ascribe this to the water of crystallization, as the melting point 167° was obtained with the substance dried at 105° used for analysis, whereas with samples which had been only air dried (or dried at 50°) we obtained melting points as low as 160–161°, that is, only 2° or 3° above the 158° obtained by Benedikt.

In order to determine whether the formation of the trinitrophloroglucine and its diethylether was due to a direct reaction, or to the secondary reaction on the trinitrophloroglucine triethylether of some sodic hydrate formed by the moisture of the air acting on the sodic ethylate, the following experiment was tried. Absolute alcohol made in the usual way with quick-lime was treated with a small quantity of sodium, and then the unaltered alcohol distilled off from the sodic alcoholate in a perfectly dry apparatus, which communicated with the outer air only through a drying tube; to the distillate in the flask which served as a receiver, a quantity of bright sodium was added as quickly as possible, after which it was closed at once with a cork carrying a drying tube. When the reaction was at an end, and the solution of sodic ethylate had cooled, 5 gr. of dry tribromtrinitrobenzol were added, and the mixture allowed to stand over night closed with the cork carrying the drying tube. The solution, which had turned red, was acidified with dilute sulphuric acid and allowed to evaporate spontaneously, when after purification it yielded 2 gr. of the triethylether of trinitrophloroglucine instead of 0.12 gr., the usual yield when no special precautions were taken to exclude atmospheric moisture. It is evident, therefore, that the trinitrophloroglucine triethylether is formed at first, and afterward saponified wholly or in part by sodic hydrate produced by the action of moisture on the sodic ethylate. That most of this sodic hydrate is formed during the spontaneous evaporation of the alkaline solution was shown by two experiments, in which the triethylether of trinitrophloroglucine was treated with a solution of sodic ethylate, with all the precautions described above, except that in one of these experiments the alkaline liquid was allowed to evaporate spontaneously, when all the triethylether was saponified, the whole product being soluble in water, whereas in the other, which was acidified before evaporating, 0.65 gr. of unaltered triethylether was recovered, 0.7 gr. having been the amount used.

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* The percentages of carbon and hydrogen are as near to those required by the formula as could be expected when the difficulty of making a combustion of this explosive substance is considered.

Lobry de Bruyn* has encountered similar difficulties in studying the action of sodic ethylate upon the unsymmetrical trinitrobenzol (1, 2, 4), as in this case considerable quantities of dinitrophenol were obtained, whereas with sodic methylate the dinitroanisol was the only organic product.

Experiments with Acetic Ester as the Solvent.

After we had found that the presence of benzol diminished the tendency of sodic ethylate to replace nitro groups in the tribromtrinitrobenzol, we tried some experiments on the action of other solvents. The choice here however was limited, because there are so few liquids belonging to a different class from benzol which have any considerable solvent action on the tribromtrinitrobenzol; in fact, acetone and acetic ester were the only ones easily obtained which fulfilled this condition, and acetone had to be rejected, as it seemed to take part in the reaction, giving a dark brownish red solution, very different from the orange-red obtained in all other cases. This result was not unexpected after the work of Freer,† published only in the preliminary paper at the time we tried this experiment, and since we did this work we have seen the paper of Janovsky,‡ describing the colors which he obtained by the action of acetone and potassic hydrate on dinitro compounds of the aromatic series.

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* Rec. Trav. Chim. des Pays-Bas, IX. 191.

† Am. Chem. Journ., XII. 355; XIII. 308, Freer and Higley; XIII. 322.

‡ Ber. d. ch. Ges., 1891, p. 971.

In our first experiment with acetic ester we used the commercial article without specially drying it. The action was carried on in the usual way, 5 gr. of tribromtrinitrobenzol being used. The aqueous washings gave tests for nitrite and bromide, but the organic product was found to consist principally of the tribromdinitrophenetol melting at 147°, described in our previous paper.* For greater certainty it was analyzed, with the following results: —

I. 0.2972 gr. of the substance gave by the method of Carius 0.3721 gr. of argentic bromide.

II. 0.2788 gr. of the substance gave 0.3535 gr. of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found.	
		I.	II.
Bromine	53.46	53.27	53.96

This experiment called our attention to a subject which we had already studied without any very definite result, that is, the conditions under which the phenetol $C_6Br_3(NO_2)_2OC_2H_5$ is formed, rather than the tribromnitroresorcine diethylether, $C_6Br_3NO_2(OC_2H_5)_2$. Our previous work had led us to the conclusion that the presence of a trace of water is favorable to the formation of the phenetol, as on one occasion when benzol not dried over sodium was used this substance was obtained, and in the experiment described in our previous paper which yielded a quantity of the phenetol common benzol was also used, whereas in all the preparations made by us with absolute benzol and alcohol not a trace of the phenetol has been found. On the other hand, in a repetition of the experiment with common benzol, and in one in which undried benzol and common instead of absolute alcohol were used only the resorcine ether $C_6Br_3NO_2(OC_2H_5)_2$ was isolated. To test this question still further, we repeated the experiment described at the beginning of this section, using carefully dried acetic ester instead of the commercial article, and obtained decidedly less of the phenetol with a large proportion of the tribromnitroresorcine diethylether, thus confirming, although not absolutely proving, our previous inference that the presence of a trace of moisture is favorable to the formation of the phenetol.

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* These Proceedings, XXV. 185.

Action when Alcohol is the only Solvent used.

This action has been already described in our first paper, but after we had found, as described in the preceding sections, that the action when benzol was present took place in the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3\,NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3\,NaBr,$$
$$C_6Br_3(NO_2)_3 + 2\,NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2\,NaNO_2,$$

it became of interest to determine whether the first of these reactions took place if alcohol was the only solvent, or whether the action consisted of the second alone, as we had supposed when we published our first paper. A very little work was sufficient to prove the presence of the trinitrophloroglucine triethylether, or the phenols formed by its saponification, among the products of the reaction when alcohol was the only solvent, thus showing that the action in the two cases is parallel, although the first reaction takes place to a much more limited extent when alcohol is the only solvent, than when a mixture of alcohol and benzol is used. Our attempts to determine the relative amounts of the products of each of these two reactions are described in a later section.

Preparation of Tribromnitroresorcine Diethylether and Trinitrophloroglucine Triethylether.

It follows from what has been said in the preceding sections, that the best way to prepare tribromnitroresorcine diethylether is to allow tribromtrinitrobenzol (10 parts) to stand in the cold for twelve hours with an alcoholic solution of sodic ethylate (from 1.5 parts of sodium), then, after the solvent has evaporated spontaneously, to wash the residue with water, and after one crystallization of the insoluble part from alcohol treat it in the cold with an alcoholic solution of sodic hydrate for about twelve hours to saponify the trinitrophloroglucine triethylether also present. The sodium salt thus formed is washed out, and the residue crystallized from alcohol until it shows the melting point of 101°.

If, on the other hand, trinitrophloroglucine triethylether is to be prepared, the tribromtrinitrobenzol should be dissolved in anhydrous benzol (dried with sodium) and the alcoholic solution of sodic ethylate added to this solution. Every precaution should be taken to exclude even traces of moisture, and after the twelve hours standing the solution should be acidified with dilute sulphuric acid before allowing it to evaporate spontaneously. The residue, after washing with water, is purified by crystallization from alcohol, which separates the two ethers formed by the parallel reactions.

Quantitative Study of the Action of Sodic Ethylate on Tribromtrinitrobenzol.

After we had proved that this action takes place in these two different ways,

$$C_6Br_3(NO_2)_3 + 3\ NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3\ NaBr,$$
$$C_6Br_3(NO_2)_3 + 2\ NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2\ NaNO_2,$$

it became of interest to determine the relative extent of each of the parallel reactions under varying conditions, and the easiest way to do this was obviously to find the amount of sodic bromide and sodic nitrite formed, as the first must have proceeded from the reaction giving the trinitrophloroglucine triethylether, the second from that producing the tribromnitroresorcine diethylether. In addition to this we have weighed the amount of organic matter formed, and have made some not very successful attempts to determine the amount of its several constituents. The method adopted was the following. A weighed quantity of tribromtrinitrobenzol mixed with the solvent and the ethylate in the proportion of three atoms of sodium to each molecule stood over night in a corked flask. The liquid was then allowed to evaporate spontaneously, and the residue washed thoroughly with water. The weight of the organic matter insoluble in water was taken, and also that of the aqueous solution which contained all the sodium salts; this was then divided into weighed parts, one of which was acidified with nitric acid, and after filtering out and weighing the diethylether of trinitrophloroglucine the amount of sodic bromide it contained was determined with argentic nitrate. The second portion of the aqueous liquid was used for the determination of the amount of sodic nitrite, but it was not easy to find a method which would be applicable in this case. The common way of determining a nitrite with potassic permanganate was inadmissible, because of the presence of organic matter. The urea method in its usual form was also inapplicable because of the presence of sodic carbonate, but finally by modifying it in the following way we succeeded in obtaining satisfactory results. The weighed portion of the solution to be tested, mixed with a sufficient quantity of urea, was poured into a little flask, and a small test-tube containing dilute sulphuric acid put into the flask supported in a vertical position by a piece of platinum wire projecting from its upper end and resting against the neck of the flask. The apparatus was then filled with carbonic dioxide from a heated tube containing magnesite, after which by shaking the flask the sulphuric acid was added to its contents in small quantities at a time, and the nitrogen given off collected over a solution of potassic hydrate, and measured in the usual way. It is necessary to heat the flask gently toward the end of the operation to drive off all the nitrogen. One half of the nitrogen collected is derived from the sodic nitrite. To test the accuracy of the method two determinations of the nitrogen in commercial sodic nitrite were made by it which gave, —

	Found.	
Nitrogen	18.09	18.11

and as they agreed with each other, and came tolerably near to the usual percentage of nitrogen in commercial sodic nitrite (between 19 and 20 per cent), it was evident that the method was accurate enough for our purposes. A third portion of the aqueous liquid was in two experiments used for the determination of the trinitrophloroglucine, but we give our results with a great deal of hesitation, as we were unable to find any satisfactory quantitative method; methods based upon extraction with an organic solvent, or the precipitation of the barium salt, which Benedikt says is insoluble, led to no result. We were therefore driven to determining the amount of nitrogen in the residue obtained by evaporating to dryness a portion of the aqueous solution acidified with sulphuric acid, and calculating from this the amount of trinitrophloroglucine, on the assumption, which at best can be but approximately correct, that this was the only substance containing nitrogen left in the residue.

Experiments in which Alcohol was the only Solvent used. — I. Weight taken, 10.556 gr. Weight of aqueous solution, 135.4 gr.; 8.6 gr. of the solution gave 16.9 c.c. of nitrogen from the sodic nitrite under a temperature of 23° and a pressure of 763.8 mm.; 28.2 gr. of the solution gave 1.1718 gr. of argentic bromide; 20.8 gr. of the solution gave after the nitrous acid had been expelled by sulphuric acid 8.2 c.c. of nitrogen at a temperature of 23° and a pressure of 767.8 mm.; 54.4 gr. of the solution gave 0.808 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 6.97 gr.

II. Weight taken, 10.1582 gr. Weight of aqueous solution, 164.55 gr.; 15.95 gr. of the solution gave 24.65 c. c. of nitrogen from the sodic nitrite at a temperature of 26°.5, and a pressure of 765 mm.; 58.45 gr. of the solution gave 1.6583 gr. of argentic bromide, and yielded 0.8499 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 5.78 gr.

III. Weight taken, 1.0366 gr. Weight of aqueous solution, 121.4 gr.; 62.5 gr. of the solution gave 13.6 c. c. of nitrogen from the sodic nitrite at a temperature of 21° and a pressure of 765.2 mm.; 58.9 gr. of the solution gave 0.2700 gr. of argentic bromide. The organic matter insoluble in water weighed 0.48 gr.

IV. Weight taken, 10 gr.* Weight of aqueous solution 142.9 gr.; 13.7 gr. of the solution gave 25.7 c.c. of nitrogen from the sodic nitrite at a temperature of 29°.5 and a pressure of 759.2 mm.; 55.1 gr. of the solution gave 1.9029 gr. of argentic bromide; 1.7 gr. of the diethylether of trinitrophloroglucine were obtained from the 10 gr. used. The weight of organic matter insoluble in water was 6.4 gr.

V. Weight taken, 10 gr.* Weight of aqueous solution, 114.8 gr.; 14.6 gr. of the solution gave 32.3 c.c. of nitrogen from the sodic nitrite at a temperature of 28° and a pressure of 764.1 mm.; 48.7 gr. of the solution gave 0.9573 gr. of argentic bromide; 2.4 gr. of the diethylether of trinitrophloroglucine were obtained from the 10 gr. used. The weight of organic matter insoluble in water was 5.6 gr.

The results of these experiments are given in tabular form at the end of the next section.

Experiments in which Benzol was the Principal Solvent used.— VI. Weight taken, 10.0220 gr. Weight of aqueous solution, 126.65 gr.; 11.7 gr. of the solution gave 17.15 c. c. of nitrogen from the sodic nitrite at a temperature of 24° and a pressure of 764.5 mm.; 28.7 gr. of the solution gave 1.6952 gr. of argentic bromide; 24.7 gr. of the solution gave after the nitrous acid had been expelled by sulphuric acid 12.2 c. c. of nitrogen at a temperature of 25° and a pressure of 766.1 mm. The acid precipitated from these 24.7 gr. of the solution 0.3374 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 4.99 gr.

VII. Weight taken, 10.1976 gr. Weight of aqueous solution, 135.2 gr.; 19.3 gr. of the solution gave 27.2 c. c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 750.9 mm.; 43.9 gr. of the solution gave 1.6158 gr. of argentic bromide; 72 gr. of the solution gave 1.4724 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 5.51 gr.

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* This weight is accurate only to tenths of a gram.

VIII. Weight taken, 1.2524 gr. Weight of aqueous solution, 37.3 gr.; 24.2 gr. of the solution gave 14.3 c.c. of nitrogen from the sodic nitrite at a temperature of 19° and a pressure of 771.5 mm.; 13.1 gr. of the solution gave 0.4097 gr. of argentic bromide. The organic matter insoluble in water weighed 0.55 gr.

IX. Weight taken, 1.2682 gr. Weight of the aqueous solution, 38.1 gr.; 19.7 gr. of the solution gave 12 c.c. of nitrogen from the sodic nitrite at a temperature of 24° and a pressure of 767.3 mm.; 18.4 gr. of the solution gave 0.5082 gr. of argentic bromide. The organic matter insoluble in water weighed 0.58 gr.

X. Weight taken, 1.2287 gr. Weight of the aqueous solution, 53.65 gr.; 17.65 gr. of the solution gave 7.7 c. c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 766.1 mm.; 18.9 gr. of the solution gave 0.2664 gr. of argentic bromide, and 0.0854 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 0.68 gr.

In the following tables the first column gives the number of the experiment, and the weight of tribromtrinitrobenzol used; the second, the percentage of nitrogen removed as sodic nitrite referred to the total amount of nitrogen which could be removed from the tribromtrinitrobenzol by this reaction, that is, two out of the three atoms of nitrogen, because the product $C_6Br_3NO_2(OC_2H_5)_2$ contains one nitro group; the third column gives the percentage of the total bromine removed as sodic bromide; the fourth, the weight of the organic matter insoluble in water; the fifth, the weight of the diethylether of trinitrophloroglucine; and the sixth, the weight of trinitrophoroglucine calculated from the volume of nitrogen obtained from the residue after acidification with sulphuric acid.

TABLE I.—ACTION OF SODIC ETHYLATE IN ETHYL ALCOHOL.

	Weight of $C_6Br_3(NO_2)_3$ used.	Per Cent of Nitrogen.	Per Cent of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH(NO_2)_3$	Weight of $C_6(OH)_3(NO_2)_3$
I.	10.556	45.88	42.53	6.97	2.0	0.38
II.	10.1582	44.85	36.67	5.78	2.39	
III.	1.0366	46.95	42.85	0.48		
IV.	10.	46.86	39.39	6.4	1.7	
V.	10.	45.06	18.02	5.6	2.4	

TABLE II. — ACTION OF SODIC ETHYLATE WITH BENZOL AND ALCOHOL.

	Weight of $C_6Br_3(NO_2)_3$	Per Cent of Nitrogen.	Per Cent of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH(NO_2)_3$	Weight of $C_6(OH)_3(NO_2)_3$
VI.	10.022	33.58	59.54	4.99	1.73	0.44
VII.	10.1976	33.09	38.91	5.51	2.8	
VIII.	1.2524	33.03	74.32	0.55		
IX.	1.2682	33.31	66.21	0.58		
X.	1.2287	34.42	49.10	0.68		

An examination of these tables shows that the percentages of nitrogen removed are fairly constant under each set of conditions, the maximum differences being, in Table I., 2.1 per cent, in Table II., 1.39 per cent, — which are surprisingly small when the nature of the process and the roughness of the manipulations are considered. These numbers, therefore, are well fitted to give an idea of the effect on the reactions of the presence of benzol, and they show that it diminishes the amount of sodic nitrite formed, since the percentage of nitrogen removed when alcohol alone is present averages 45.92 (maximum 46.95, minimum 44.85), whereas if the solvent is partly benzol the average percentage falls to 33.49 (maximum 34.42, minimum 33.03).

On the other hand, no agreement is found in the amounts of bromine removed as sodic bromide, the maximum difference in Table I. being 24.83 per cent, in Table II. 35.41 per cent; but in spite of this these results show that the presence of benzol favors the removal of bromine, since of the five determinations of bromine in presence of benzol (Table II.), only one (38.91 per cent) is below the largest percentage of bromine obtained (42.85 per cent) when alcohol was the only solvent (Table I.), and most of those in Table II. are very far above those in Table I.

As to the numerical relations between the percentages of inorganic compounds formed under the two sets of conditions, it is to be observed that in the alcohol series the amounts of nitrite and bromide are approximately equal. In the benzol series the amount of nitrite is almost exactly one third of the total amount which could have been formed, and is in some cases about one half that of the bromide. In most cases, between 80 and 90 per cent of the tribromtrinitrobenzol used is accounted for by the amounts of inorganic salts formed. The experimental work is not accurate enough to allow a more careful discussion of this part of the subject, as not enough attention was paid to various details, such, for instance, as maintaining a constant temperature, and measuring accurately the amounts of solvent used.

In all the experiments with benzol given in Table II. free alcohol was also present. To determine what influence this had on the reaction, we made another experiment, in which all free alcohol was carefully excluded, so that in this case benzol was the only liquid present.

XI. Weight taken, 5.0453 gr. Weight of the aqueous solution, 83.4 gr.; 19.6 gr. of the solution gave 23.8 c. c. of nitrogen at a temperature of 28°.5 and a pressure of 760.1 mm.; 43.4 gr. of the solution gave 1.9610 gr. of argentic bromide and 1.55 gr. of the diethylether of trinitrophloroglucine. The organic matter insoluble in water weighed 2.75 gr.

From these results 35.34 per cent of nitrogen and 59.62 per cent of bromine are obtained. The percentage of nitrogen, when benzol and alcohol were used as the solvents, averaged 33.49, so that this experiment shows that the presence of alcohol does not materially affect the result. The somewhat high percentage of nitrogen in this experiment may be due to the fact that the mixture stood two days instead of the usual twelve hours. This subject of the effect of time on the action will be discussed later in the paper.

We have also made two quantitative determinations, in which acetic ester was used with a little alcohol as the solvent.

XII. Weight taken, 1.0412 gr. Weight of the aqueous solution, 58 gr.; 17.5 gr. of the solution gave 0.63 c.c. of nitrogen at a temperature of 23°.5 and a pressure of 758.9 mm.; 40.5 gr. of the solution gave 0.4504 gr. of argentic bromide.

XIII. Weight taken, 1.0271 gr. Weight of the aqueous solution, 49.1 gr.; 18 gr. of the solution gave 2.8 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 760.8 mm.; 31.1 gr. of the solution gave 0.4902 gr. of argentic bromide.

	Per Cent of Nitrogen.	Per Cent of Bromine.
XII. 1.0412	3.62	50.06
XIII. 1.0271	13.49	60.15

We are inclined to regard No. XII. with suspicion; but No. XIII. alone shows that acetic ester has an even more unfavorable influence than benzol on the formation of the sodic nitrite; this is probably due to the fact that in this case there is a tendency to form the tribromdinitrophenetol, which would yield half as much sodic nitrite as the tribrommononitroresorcine diethylether formed when benzol was used.

Relative Yields of the Organic Products. — After we had determined the amounts of sodic bromide and nitrite formed by the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3\,NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3\,NaBr,$$
$$C_6Br_3(NO_2)_3 + 2\,NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2\,NaNO_2,$$

we tried to get an idea of the relative yields of the organic products. This could be done with some approach to accuracy in the case of the reaction which produces sodic bromide, because during the work most of the trinitrophloroglucine triethylether was converted into the salts of trinitrophloroglucine or its diethylether, both of which can be easily separated from the other organic products on account of their solubility in water. With the tribromnitroresorcine diethylether on the other hand, no such approach to accuracy was obtained, because it could be purified only by crystallization, and a large portion of it remained mixed with the viscous impurity already mentioned. To obtain the following results, the organic matter insoluble in water obtained from two experiments was repeatedly crystallized from alcohol, until as much pure tribromnitroresorcine diethylether and trinitrophloroglucine triethylether had been obtained as possible. To the amount of the latter, which was very small, were added the calculated amounts of the triethylether corresponding to the quantities found of free trinitrophloroglucine and its diethylether. Two pairs of experiments were studied in this way, one from the series in which alcohol was the only solvent, and one from that in which benzol was used.

Experiments I. and II. — Alcohol the only solvent. 20.71 gr. of tribromtrinitrobenzol gave 12.75 gr. of organic matter insoluble in water, from which were obtained 5.11 gr. of $C_6Br_3NO_2(OC_2H_5)_2$, 1.4 gr. of the same slightly impure, 5.1 gr. of the semi-liquid fraction from the mother liquor, and 0.49 gr. of $C_6(OC_2H_5)_3(NO_2)_3$. From the aqueous solution 4.39 gr. of $C_6OH(OC_2H_5)_2(NO_2)_3$ were obtained, corresponding to 4.77 gr. of the triethylether, and

0.78 gr.* of $C_6(OH)_3(NO_2)_3$, corresponding to 1.03 gr. of the triethylether, making the total yield of the triethylether 6.29 gr.

Experiments VI. and VII. — Benzol present, 20.21 gr. of tribromtrinitrobenzol gave 10.50 gr. of organic matter insoluble in water from which were obtained 3.25 gr. of $C_6Br_3NO_2(OC_2H_5)_2$, 1.36 gr. of $C_6(OC_2H_5)_3(NO_2)_3$, and somewhat less than 6 gr. of the semi-liquid fraction from the mother liquors. From the aqueous solution were obtained 4.53 gr. of $C_6OH(OC_2H_5)_2(NO_2)_3$, corresponding to 4.93 gr. of the triethylether, and 0.88 gr.* of $C_6(OH)_3(NO_2)_3$, corresponding to 1.16 gr. of the triethylether, making the total yield of the triethylether 7.45 gr.

These results confirm the inference drawn from the percentage, of sodic nitrite and bromide, that the presence of benzol is unfavorable to the reaction by which sodic nitrite is formed, but promotes that which yields sodic bromide; a fact which is shown more plainly by this collection of the results in tabular form.

	$C_6(OC_2H_5)_3(NO_2)_3$.	$C_6Br_3NO_2(OC_2H_5)_2$
Alcohol alone (I. and II.)	6.29 gr.	5.11†
Benzol and alcohol (VI. and VII.)	7.45 gr.	3.25†

All our results, therefore, show that the presence of benzol is favorable to the elimination of bromine, unfavorable to that of nitro groups. The most probable theoretical explanation of this observation which has occurred to us depends on the effect of the change of solvents upon the amounts of the salts precipitated, but any discussion of this theory at present would not be worth while, because the principle on which it rests has not been tested by experiment so far as we can find.

We have not succeeded in finding the cause of the very marked variations in the amounts of sodic bromide shown in Tables I. and II. At first we feared they might be due to defects in our experimental work, but that this is not the case is shown by the following comparison of the weights of trinitrophloroglucine triethylether actually found with the amounts of this substance calculated from the percentages of bromine eliminated as sodic bromide in the same experiment. We have selected this body for the comparison, because, as has been already stated, these weights were determined with a fair degree of accuracy.

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* These numbers are only estimates, as the amounts of trinitrophloroglucine were determined only in Nos. I. and VI., the weight found being doubled to give the numbers. It is to be remembered also that our method for determining the trinitrophloroglucine was far from satisfactory.

† These numbers are only approximations to the true yields.

	Calculated	Found.
Alcohol alone (I. and II.)	6.30	6.29
Alcohol and benzol (VI. and VII.)	7.62	7.45

The agreement is much closer than we had any right to expect, and shows that the differences in the percentages of bromine are due to absolute variations in the extent of the reaction by which the bromine is removed, since experiments VI. and VII. differ in this respect very widely (VI. 59.54 per cent of bromine, VII. 38.91 per cent of bromine); and yet the amount of the trinitrophloroglucine triethylether calculated from these different percentages of bromine corresponds almost exactly to that obtained experimentally.

PART II.

ACTION OF OTHER ALCOHOLATES ON TRIBROMTRINITROBENZOL.

In addition to the work with sodic ethylate just described, we have tried the action of the sodium compounds of other alcohols on the tribromtrinitrobenzol, and give in the first place descriptions of the new compounds thus obtained, followed by a series of quantitative experiments similar to those tried with the ethylate.

Sodic Methylate.

The organic compound insoluble in water obtained by the action of sodic methylate on tribromtrinitrobenzol consisted in every experiment we have tried of the tribromnitroresorcine dimethylether, melting at 126°, and already described in our first paper;* as, however, we found that a considerable amount of sodic bromide was formed in these experiments, we turned our attention to the aqueous washings of this organic matter, in which it was evident that the product formed by the removal of the bromine was to be sought. Upon acidifying this aqueous solution with dilute sulphuric acid, a copious precipitate was obtained, which was only slightly soluble in water, and was purified by crystallization with the following precautions. The substance was dissolved in as small a quantity as possible of cold alcohol, water was then added until it began to grow turbid, when the solution was cleared by the addition of a drop or two of alcohol, and allowed to evaporate spontaneously, all these operations being carried on in the cold. When it showed the constant melting point 77–78°, it was dried and analyzed with the following results: —

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* These Proceedings, XXV. 186.

0.2298 gr. of the substance gave on combustion 0.2792 gr. of carbonic dioxide and 0.0597 gr. of water.

	Calculated for $C_6(OCH_3)_2OH(NO_2)_3$.	Found.
Carbon	33.22	33.13
Hydrogen	2.42	2.89

To confirm this result the sodium salt was made and analyzed; for this purpose 1 gr. of the substance was treated with 0.1 gr. of sodic hydrate dissolved in a little water, that is, decidedly less sodic hydrate than would be needed to convert the whole of the substance into its salt. The yellow solution thus obtained was evaporated to dryness at 100°, washed with benzol to remove the small quantity of the free phenol which had dissolved in the water, dried at 100°, and analyzed with the following result: —

0.3730 gr. of the salt gave 0.0874 gr. of sodic sulphate.

	Calculated for $C_6(OCH_3)_2ONa(NO_2)_3$.	Found
Sodium	7.39	7.59

These analyses and the analogy with the corresponding ethyl compound leave no doubt that the substance is the dimethylether of trinitrophloroglucine.

Properties of the Dimethylether of Trinitrophloroglucine, $C_6(OCH_3)_2OH(NO_2)_3$. — The substance crystallizes with the precautions given above in long slender needles, with a slightly yellowish tinge, which melt at 77–78°, and are very soluble in ethyl alcohol, methyl alcohol, ether, benzol, chloroform, acetone, or glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroine; somewhat soluble in cold water, more soluble in hot. With alkalies it forms reddish yellow salts. Strong sulphuric or hydrochloric acid does not act on it; it dissolves in strong nitric acid, but seems to be precipitated unchanged by dilution.

We also obtained a small amount of another substance with a higher melting point, but not in sufficient quantity to characterize it.

Action of Sodic Propylate on Tribromtrinitrobenzol.

4 gr. of normal propyl alcohol were mixed with anhydrous benzol, and treated with 1.5 gr. of metallic sodium until all the sodium had disappeared; the reaction ran slowly, and was assisted by a gentle heat. The sodic propylate thus obtained was carefully cooled, and then a benzol solution of 10 gr. of tribromtrinitrobenzol added in small portions at a time, shaking and cooling with water after each addition. The proportions are about three atoms of sodium and three molecules of propyl alcohol to each molecule of tribromtrinitrobenzol. As the first portions of the solutions were mixed the liquid turned blood-red, and this color, which at first faded to yellow on shaking, became permanent as more of the solution of tribromtrinitrobenzol was added. The mixture, which at no time showed a rise of temperature, was allowed to stand over night in a corked flask, and then the solution was filtered from a deposit of solid matter, which, after drying off the benzol, gave tests for a bromide and a nitrite. The benzol solution to which the solid not used for the above tests had been added was treated with water, and then acidified with dilute sulphuric acid, washed thoroughly, and, after most of the benzol had been recovered by distillation, the rest was distilled off in a current of steam. The residue thus obtained was oily, but solidified after standing for some time; it was then purified by crystallization from alcohol until it showed the constant melting point 109–110°, when it was dried at about 70°, and analyzed with the following results: —

0.2366 gr. of the substance gave on combustion 0.4058 gr. of carbonic dioxide and 0.1214 gr. of water.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.78
Hydrogen	5.43	5.70

The substance gives no test for bromine when heated on a copper wire. These results prove that it is the normal propylether of trinitrophloroglucine.

The aqueous solution, acidified with sulphuric acid, from which the benzol had been separated gave on extraction with ether a small amount of a yellow substance, which seemed to be trinitrophloroglucine, but was not present in sufficient amount for complete identification.

Properties of the Normal Tripropylether of Trinitrophloroglucine, $C_6(OC_3H_7)_3(NO_2)_3$. — This substance crystallizes in plates often as much as three millimeters long and one broad, which under the microscope are seen to be made up of a number of flat prisms with square ends united by their longer sides, and usually much striated on lines parallel to both sets of edges. Its color is white with a very slight yellowish tinge, and it turns yellowish brown on standing exposed to the air. It melts at 109–110°, and is soluble in cold ethyl or methyl alcohol, more freely when hot; freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in ligroine, or in water whether hot or cold. Neither strong sulphuric, strong nitric, nor strong hydrochloric acid has any apparent action on it, whether cold or hot. The best solvent for it is boiling alcohol.

In another experiment no benzol was used, but the tribromtrinitrobenzol suspended in propyl alcohol was treated with sodic propylate. The product in this case was an oil which did not solidify even after standing for three months. We accordingly tried to purify it by treatment with a cold solution of sodic hydrate, and in this way obtained an orange solution, from which trinitrophloroglucine was easily isolated, pointing to the presence of the tripropyl ether of this body in the oil. After we could obtain no more of the sodium salt of the trinitrophloroglucine by further action of sodic hydrate, the oil was washed with water, dissolved in alcohol, precipitated again with water, and dried at 100°, when we hoped an analysis might throw some light on its composition; but in this we were disappointed, as a determination of the amount of bromine gave 45.29 per cent, whereas the tribromnitroresorcine dipropylether, which we hoped might have been formed, should contain 50.42 per cent. of bromine. As we could find no better way of purifying this substance, we have been forced to leave undecided the nature of the product formed by the replacement of nitro groups in tribromtrinitrobenzol by propoxy radicals. Fortunately, it is not a point of great importance.

Action of Sodic Isopropylate on Tribromtrinitrobenzol.

4 gr. of isopropyl alcohol were converted into its sodium compound by treatment with 1.5 gr. of sodium in anhydrous benzol, when it was found that the isopropyl alcohol acts on sodium more energetically than normal propyl alcohol, but both act less readily than ethyl alcohol. The isopropylate thus obtained was allowed to

act on 10 gr. of tribromtrinitrobenzol under the conditions described in the preceding section. The phenomena observed in this case were the same as those described for the normal propylate except that a slight rise of temperature from the reaction was observed. The solid deposited over night gave a strong test for sodic bromide and a distinct test for sodic nitrite. The principal organic product was obtained and purified in the way given under the normal propyl compound until it showed the constant melting point 130°, when it was dried at 100°, and analyzed with the following results: —

0.2280 gr. of the substance gave on combustion 0.3876 gr. of carbonic dioxide and 0.1182 gr. of water.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.36
Hydrogen	5.43	5.76

The substance gave no test for bromine when heated with cupric oxide. A small amount of trinitrophloroglucine seemed to be formed as a secondary product in preparing the substance analyzed above.

Properties of the Triisopropylether of Trinitrophloroglucine, $C_6(OC_3H_7)_3(NO_2)_3$. — This substance crystallizes in plates often one centimeter long, made up of flattened prisms united by their longer sides. These prisms are terminated by two planes at an obtuse angle to each other, and seem to belong to the monoclinic system. It is white when first prepared, but gradually takes on an orange color on exposure to the air. It melts at 130°, and is not very soluble in cold ethyl or methyl alcohol, more soluble in hot; very soluble in benzol or chloroform; freely in ether, or acetone; soluble in carbonic disulphide; slightly soluble in cold glacial acetic acid, freely when hot; very slightly soluble in ligroine, and nearly insoluble in water whether cold or hot. The three strong acids have no apparent action on it whether cold or hot. The best solvent for it is boiling alcohol.

Action of Sodic Benzylate on Tribromtrinitrobenzol.

The sodic benzylate used was prepared as follows. To 1.3 gr. of sodium mixed with anhydrous benzol and heated in a flask with a return condenser, 6.5 gr. of benzyl alcohol were added in small quantities at a time, and the heating continued until all the sodium had disappeared, which usually was not till after four hours. The benzyl alcohol therefore acts with sodium much more slowly than any of the other alcohols used by us. In this way we obtained a benzol * solution of the sodic benzylate, which remained clear after it had cooled until it was shaken, when the solid separated in a gelatinous state. To the mixture of gelatinous sodic benzylate and benzol thus obtained a benzol solution of 9 gr. of tribromtrinitrobenzol was added; that is, for each molecule of tribromtrinitrobenzol we used three molecules of sodic benzylate.† The mixture was allowed to stand in the cold over night, the orange-red solution thus formed evaporated to dryness on a steam radiator at temperatures below 70°, and the residue washed with water and afterward with alcohol, after which it was purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting point 171°. The analyses of the substance dried at 100° gave the following results: —

I. 0.2038 gr. of the substance gave on combustion 0.4546 gr. of carbonic dioxide and 0.0752 gr. of water.

II. 0.2678 gr. of the substance gave 18.8 c.c. of nitrogen at a temperature of 25° and a pressure of 765.3 mm.

	Calculated for $C_6(OC_7H_7)_3(NO_2)_3$.	Found.	
		I.	II.
Carbon	61.01	60.84	
Hydrogen	3.96	4.10	
Nitrogen	7.91		7.89

The substance gave no test for bromine when heated with cupric oxide.

10 gr. of tribromtrinitrobenzol gave only 1.5 gr. of the tribenzylether of trinitrophloroglucine, the analysis of which is given above, that is, less than 13 per cent of the theoretical yield. This substance, therefore, is not by any means the principal product of the reaction. What the other products are will be discussed after the description of the properties of the benzylether.

Properties of the Trinitrophloroglucine Tribenzylether. — This substance crystallizes from a mixture of alcohol and benzol in slender white needles forming a thick mat. It turns yellowish brown on exposure to the air, and melts at 171°; is slightly soluble even in hot alcohol, less soluble still in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, or acetone; freely in carbonic disulphide; soluble in glacial acetic acid; very slightly soluble in ligroine; essentially insoluble in water, whether cold or hot. The best solvent for it is a mixture of alcohol and benzol. Strong sulphuric acid does not seem to act on it until charring sets in; strong nitric acid does not act on it in the cold, but seems to oxidize it when hot; strong hydrochloric acid has no apparent action on it, hot or cold.

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* Since this part of our work was finished, Brühl and Biltz have published similar observations on other alcoholates in Ber. d. ch. Ges., XXI. 649 (1891).

† The same principal product was obtained in a subsequent experiment with only two molecules of sodic benzylate. In most cases a slight excess of benzyl alcohol was used.

Other Products of the Action of Sodic Benzylate on Tribromtrinitrobenzol.— To obtain these substances the aqueous and alcoholic washings mentioned above were evaporated to dryness, and the oily portion separated by extraction with a little alcohol from the salts. These, it was found, were a mixture of the sodium salt of trinitrophloroglucine with sodic bromide and nitrite, from which the trinitrophloroglucine was easily obtained, and identified by the melting point 167°, and by analysis. It is one of the principal products of the reaction, and in fact most of the trinitrophloroglucine used for the analyses given in the first part of this paper was obtained in this way.

The oily material separated by the alcohol consisted mostly of the excess of benzyl alcohol, but on warming it we perceived the smell of benzyl bromide, and also suffered from its violent action on the eyes. Accordingly some of it, carefully washed to remove any sodic bromide, was boiled with an alcoholic solution of sodic sulphide, when it gave a strong smell of benzyl sulphide, and the water with which it was washed gave a faint test for bromine with chlorine water. We did not succeed, however, in isolating the benzyl sulphide, which at best must have been present in very small quantity. Another similar oil, after thorough washing with water, was boiled with sodic acetate and alcohol, then water was added, which after being freed from the organic matter gave a slight test for bromine with chlorine water. In another experiment the original product, after acidification with dilute sulphuric acid, was distilled with steam, and the oily distillate, having been thoroughly washed with water, was boiled with alcoholic sodic acetate, when it yielded a very strong test for a bromide with chlorine water. These experiments have convinced us that in these three preparations a small quantity of benzyl bromide was present in the product of the reaction, although we have not succeeded in isolating the benzyl bromide itself, or one of its derivatives. This did not proceed from an impurity of benzyl bromide in the benzyl alcohol used, since after boiling it with an alcoholic solution of sodic acetate no test for sodic bromide could be obtained; it must have been formed, therefore, either in the course of the reaction, or in the subsequent processes of purification. It is barely possible that this latter supposition may account for it in the last case, where the strongest test for bromine was obtained, as this was acidified before distillation with steam, and hydrobromic acid produced by the sulphuric acid and sodic bromide might have converted some of the excess of benzyl alcohol into benzyl bromide, although this seems highly improbable, because the solution was kept throughout in a very dilute state. In the two previous cases, however, this explanation cannot apply, as no acid whatever had been added, so that no hydrobromic acid could have been formed; we are forced therefore to assume that the benzyl bromide was formed by the direct reaction and not by a secondary one, and under these circumstances the following reaction is the only one which seems to us admissible:

$$3\,C_7H_7ONa + C_6Br_3(NO_2)_3 = C_6(ONa)_3(NO_2)_3 + 3\,C_7H_7Br.$$

This is certainly very improbable, and we should add, that, when we tried to confirm it by a repetition of the experiment, we did not succeed in detecting any benzyl bromide in the product. At first sight it would seem that a reaction the reverse of that given above would be more probable, but we proved that this was not the case by a special experiment, which showed that benzyl bromide had no action on the sodium salt of trinitrophloroglucine under the conditions used by us. We may add that amyl bromide also has no action under these conditions. On the other hand, there is little doubt that the benzyl bromide, if formed by this reaction, would act on the sodic benzylate forming benzylether. Accordingly, we tried to isolate benzylether from the oily product of the reaction by distilling off the excess of benzyl alcohol; there was so little of the residue which did not pass over at 207° that it was impossible to purify it properly; such as it was, however, it gave results on analysis agreeing with those calculated for benzyl alcohol (carbon 76.70 instead of 77.78). We conclude, therefore, that if the reaction given above takes place, it is only to a very moderate extent, the principal reaction being the formation of the trinitrophloroglucine tribenzylether, which was then more or less saponified by the sodic hydrate formed by the action of atmospheric moisture on the sodic benzylate. We have not succeeded in detecting the organic substance formed by the removal of one or more nitro groups, as indicated by the appearance of sodic nitrite among the products.

Sodic Isobutylate or *Sodic Isoamylate* acted with tribromtrinitrobenzol in the same way as the alcoholates already mentioned, but the organic products insoluble in water were oily, and we did not succeed in isolating any compounds fit for analysis from them. The aqueous filtrates contained a considerable amount of the sodium salt of trinitrophloroglucine. As the subject was not of sufficient interest to repay extended work, it was abandoned.

Quantitative Study of the Action of other Alcoholates on Tribromtrinitrobenzol.

The object of this work was to make a comparison between the actions of sodic ethylate and of other alcoholates on tribromtrinitrobenzol, and for this purpose we selected the quantitative determination of the amounts of sodic nitrite formed by the reaction, since our results with the ethylate had shown that the percentage of nitrogen removed as sodic nitrite was essentially constant under the conditions used by us. The amount of bromide formed was also determined in most cases, although of little value for purposes of comparison. Accordingly the following determinations were made, the results of which, with those from sodic ethylate already described, are given together in tabular form after the descriptions of the determinations. To economize our alcohols, as we had but a small stock of some of them, we have used principally the method with benzol as a solvent.

Experiments in which the Alcohol was the only Solvent.

XIV. Weight taken. 1.0578 gr. Alcoholate used, *sodic methylate.* Weight of aqueous solution, 115.1 gr. 54.3 gr. of the solution gave 13.6 c.c. of nitrogen from the sodic nitrite at a temperature of 18° and a pressure of 758.9 mm. 60.8 gr. of the solution gave 0.3768 gr. of argentic bromide.

XV. Weight taken, 1.157 gr. Alcoholate used, *sodic propylate.* Weight of aqueous solution, 92 gr. 54.1 gr. of this solution gave 13.8 c.c. of nitrogen from the sodic nitrite at a temperature of 16° and a pressure of 775.4 mm.

XVI. Weight taken, 1.1582 gr. Alcoholate used, *sodic isobutylate.* Weight of aqueous solution, 117.5 gr. 33.1 gr. of the solution gave 5.25 c.c. of nitrogen from the sodic nitrite at a temperature of 16° and a pressure of 765.5 mm. 43.3 gr. of the solution gave 0.2390 gr. of argentic bromide.

XVII. Weight taken, 1.2696 gr. Alcoholate used, *sodic isobutylate.* Weight of aqueous solution, 56.65 gr. 19.3 gr. of the solution gave 9.4 c.c. of nitrogen from the sodic nitrite at a temperature of 29°.5 and a pressure of 756.3 mm. 15.95 gr. of the solution gave 0.2198 gr. of argentic bromide.

XVIII. Weight taken, 1.5118 gr. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution, 53.3 gr. 26.5 gr. of the solution gave 8.4 c.c. of nitrogen from the sodic nitrite at a temperature of 20° and a pressure of 762.4 mm. 26.25 gr. of the solution gave 0.3352 gr. of argentic bromide.

XIX. Weight taken, 1.5656 gr. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution 85.1 gr. 37.4 gr. of the solution gave 9.9 c.c. of nitrogen from the sodic nitrite at a temperature of 19°.5 and a pressure of 766.2 mm.

Action of Sodic Methylate in Benzol.

XX. Weight taken, 1.0892 gr. Weight of solution, 65.7 gr. 31.7 gr. gave 10.1 c.c. of nitrogen from sodic nitrite at a temperature of 22° and a pressure of 766.9 mm. 34 gr. gave 0.4212 gr. of argentic bromide. The organic matter insoluble in water weighed 0.509 gr.

XXI. Weight taken, 1.2612 gr. Weight of aqueous solution, 40.05 gr. 17.35 gr. of the solution gave 11.7 c.c. of nitrogen from the sodic nitrite at a temperature of 25° and a pressure of 758.9 mm. 22.7 gr. of the solution gave 0.4088 gr. of argentic bromide.

XXII. Weight taken, 1.1561 gr. Weight of aqueous solution, 58.9 gr. 24.3 gr. of the solution gave 10.9 c.c. of nitrogen from the sodic nitrite at a temperature of 25°.5 and a pressure of 765.4 mm. 34.6 gr. of the solution gave 0.4732 gr. of argentic bromide.

Action of Normal Sodic Propylate in Benzol.

XXIII. Weight taken, 1.2281 gr. Weight of aqueous solution, 60.85 gr. 22.75 gr. of the solution gave 8.2 c.c. of nitrogen from the sodic nitrite at a temperature of 20°.5 and a pressure of 759.4 mm. 38.1 gr. of the solution gave 0.1398 gr. of argentic bromide.

XXIV. Weight taken, 1.297 gr. Weight of aqueous solution, 71.6 gr. 19.6 gr. of the solution gave 4.6 c.c. of nitrogen from the sodic nitrite at a temperature of 30° and a pressure of 767 mm. 52 gr. of the solution gave 0.7827 gr. of argentic bromide.

Action of Sodic Isopropylate in Benzol.

XXV. Weight taken, 1.3434 gr. Weight of aqueous solution, 50.15 gr. 20 gr. of the solution gave 5.9 c.c. of nitrogen from the sodic nitrite at a temperature of 24°.5 and a pressure of 762.5 mm. 30.15 gr. of the solution gave 0.2679 gr. of argentic bromide.

Action of Sodic Isobutylate in Benzol.

XXVI. Weight taken, 1.1598 gr. Weight of aqueous solution, 59.05 gr. 27.05 gr. of the solution gave 5.2 c.c. of nitrogen from the sodic nitrite at a temperature of 23°.5 and a pressure of 759.2 mm. 32 gr. of the solution gave 0.303 gr. of argentic bromide.

XXVII. Weight taken, 1.1551 gr. Weight of aqueous solution, 79.5 gr. 22.05 gr. of the solution gave 4.2 c.c. of nitrogen from the sodic nitrite at a temperature of 27° and a pressure of 764.5 mm. 57.45 gr. of the solution gave 0.722 gr. of argentic bromide.

Action of Sodic Isoamylate in Benzol.

XXVIII. Weight taken, 1.4427 gr. Weight of aqueous solution, 85.55 gr. 31.7 gr. of the solution gave 5.7 c.c. of nitrogen from the sodic nitrite at a temperature of 23° and a pressure of 760.9 mm. 40.65 gr. of the solution gave 0.4184 gr. of argentic bromide.

XXIX. Weight taken, 1.4485 gr. Weight of aqueous solution, 106.65 gr. 33.6 gr. of the solution gave 5.3 c.c. of nitrogen from the sodic nitrite at a temperature of 25°.5 and a pressure of 764.2 mm. 73.05 gr. of the solution gave 0.8515 gr. of argentic bromide.

Action of Sodic Benzylate in Benzol.

XXX. Weight taken, 1.0747 gr. Weight of aqueous solution, 92.2 gr. 33.5 gr. of the solution gave 2.7 c.c. of nitrogen from the sodic nitrite at a temperature of 30°.5 and a pressure of

758.8 mm. 58.7 gr. of the solution gave 0.5584 gr. of argentic bromide.

Action of Sodic Phenylate in Benzol.

XXXI. Weight taken, 1.1227 gr. Weight of aqueous solution, 67.15 gr. 32.5 gr. of the solution gave 3 c.c. of nitrogen from the sodic nitrite at a temperature of 29° and a pressure of 766.5 mm. 30.05 gr. of the solution gave 0.1568 gr. of argentic bromide.

The results of these experiments are collected in Tables III. and IV. with those previously given by sodic ethylate. The first column contains the sort of alcohol used and the number of the experiment, the second the weight of tribromtrinitrobenzol used, the third the percentage of nitrogen, and the fourth the percentage of bromine removed, calculated in the way already described in connection with Tables I. and II.

TABLE III. — EXPERIMENTS WITH THE ALCOHOL ALONE.

Sort of Alcohol used		Weight of Tribromtrinitro-benzol.	Percentage of Nitrogen	Percentage of Bromine.
Methyl	XIV.	1.0578	50.52	53.79
Ethyl	I.	10.556	45.88	42.53
	II.	10.1582	44.85	36.67
	III.	1.0366	46.95	42.85
	IV.	10.	46.86	39.39
	V.	10.	45.06	18.02
Propyl	XV.	1.157	38.80	
Isobutyl	XVI.	1.1582	30.40	44.69
	XVII.	1.2696	37.83	49.04
Isoamyl	XVIII.	1.5118	20.62	36.16
	XIX.	1.5656	26.73	

TABLE IV. — EXPERIMENTS WITH ALCOHOL AND BENZOL.

Sort of Alcohol used.		Weight of Tribromtrinitrobenzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XX.	1.089	35.28	59.62
	XXI	1.261	38.37	45.64
	XXII.	1.156	41.17	55.59
Ethyl	VI.	10.022	33.58	59.54
	VII.	10.1976	33.09	38.91
	VIII	1.2524	33.03	74.32
	IX	1.2682	33.31	66.21
	X.	1.2287	34.42	49.10
Propyl	XXIII.	1.2281	32.74	14.51
	XXIV.	1.297	22.83	66.30
Isopropyl	XXV.	1.3434	19.87	26.46
Isobutyl	XXVI.	1.1598	17.68	38.46
	XXVII.	1.1551	23.41	69.01
Isoamyl	XXVIII	1.4427	19.33	48.70
	XXIX.	1.4485	20.89	68.50
Benzyl	XXX.	1.0747	12.00	65.09
Phenol	XXXI.	1.1227	9.78	24.90

An examination of Tables III. and IV. shows that the percentages of nitrogen obtained with the ethylate are the only ones which agree among themselves, the numbers with other alcoholates often differing by about six per cent, in one case by nearly ten per cent. Under these circumstances it is obviously unwise to attempt to draw any definite inferences from these results; we therefore dismiss them with the general remark that the amount of nitrogen removed seems to show a tendency to diminish as the molecular weight of the alcohol increases.

The length of time during which the mixture of tribromtrinitrobenzol and the alcoholate stood seemed to have but little influence on the reaction, as is shown by Experiments V., XXIV., XXVII., and XXIX., in which the mixture stood one or more days longer than the eighteen hours used for the other experiments. In fact, longer standing could not have any great effect in the case of the ethylate, as in eighteen hours eighty to ninety per cent of the tribromtrinitrobenzol had entered into the reactions. With the higher alcoholates this was not the case, and it may be that the action had not reached its end in eighteen hours, and that the variation observed in the percentages was due to differences in the times of reaction; but some experiments, in which the mixtures were allowed to stand a longer time in order to test this point, gave unsatisfactory results, apparently on account of the oxidation of the sodic nitrite formed by the oxygen of the air.

PART III.

ACTION OF SODIC ETHYLATE ON CERTAIN DERIVATIVES OF TRIBROMTRINITROBENZOL CONTAINING ALKYLOXY RADICALS.

Action of Sodic Ethylate on the Triphenylether of Trinitrophloroglucine.

This work was undertaken in the hope that the triphenylether of trinitrophloroglucine, $C_6(OC_6H_5)_3(NO_2)_3$, might behave toward sodic ethylate like tribromtrinitrobenzol, that is, lose one or more nitro groups as sodic nitrite, which would be replaced by the ethoxy group. This hope, however, has not been fulfilled, as instead of the nitro groups the phenoxy radicals are removed by the sodic ethylate, becoming replaced by ethoxy groups, while sodic phenylate is formed. The experiments were carried on as follows. 2.5 gr. of the triphenylether of trinitrophloroglucine* dissolved in benzol were mixed with the sodic ethylate from 0.4 gr. of sodium, and the bright red mixture allowed to stand two or more hours in the cold. After this it was allowed to evaporate spontaneously, and the residue warmed with water on the steam bath, when most of it dissolved. The insoluble portion was purified by crystallization from alcohol until it showed the constant melting point 119–120°, which indicated that it was trinitrophloroglucine triethylether, and this was proved to be the case by the following analysis: —

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* In preparing this substance from tribromtrinitrobenzol again we have found that a tolerable excess of sodic phenylate should be used in order to avoid the formation of a compound containing bromine, — $C_6(OC_6H_5)_2Br(NO_2)_3$ probably. With such an excess, the reaction runs without heat, and is complete in a few minutes. We have not observed the green color noticed by us last year (these Proceedings, XXV. 188), which must therefore have been due to some impurity.

0.2080 gr. of the substance gave 22.5 c.c of nitrogen at a temperature of 21° and a pressure of 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.*
Nitrogen	12.17	12.30

The aqueous filtrate which contained the other products of the reaction beside the trinitrophloroglucine triethylether gave no test for sodic nitrite, even with starch paste, potassic iodide, and sulphuric acid. It was acidified with dilute sulphuric acid and extracted with ether, which left an oily substance solidifying after some time, and smelling strongly of phenol. To prove that this was phenol, it was dissolved in a large quantity of water and bromine water added to the solution, which gave a white precipitate melting constant after crystallization from dilute alcohol at 92°, the melting point given by Post for tribromphenol; as however both Körner and Sintenis give 95°, we thought it necessary to analyze the substance, which was done with the following result: —

0.2803 gr. of the substance gave according to the method of Carius 0.4748 gr. of argentic bromide.

	Calculated for $C_6H_2Br_3OH$.	Found.
Bromine	72.51	72.07

There can be no doubt, therefore, that the substance is tribromphenol, and that the action of the sodic ethylate upon trinitrophloroglucine triphenylether takes place according to the following reaction:

$$C_6(OC_6H_5)_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaOC_6H_5.$$

The bright red color observed in the solution was undoubtedly due to some of the sodium salt of trinitrophloroglucine formed by the action of the small amount of sodic hydrate, which it is almost impossible to exclude from sodic ethylate owing to the hygroscopic nature of absolute alcohol.

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* This analysis has also been given earlier in this paper, where the composition of the triethylether is first determined.

This decomposition of the trinitrophloroglucine triphenylether by sodic ethylate calls to mind the behavior of esters with another alcohol and a small quantity of an alcoholate, as studied by Purdy[*] and Peters,[†] especially as our ether approaches the esters on account of the marked acid properties of the trinitrophloroglucine. Kossel and Krüger[‡] have also found that sodic ethylate converts salol into salicylic ester (or acid), and sodic phenylate, and that glycerids are decomposed by sodic ethylate in a similar way, a result which is confirmed by Obermüller.[§]

Action of Sodic Ethylate on Tribromnitroresorcine Diethylether.

Early in our work with the tribromnitroresorcine diethylether melting at 101° we noticed that, although it was not acted on by a cold solution of sodic ethylate in alcohol, it was attacked if heated with such a solution, but our attempts to study this reaction were baffled for a long time by the difficulty in removing from the crystalline product the large amount of tarry matter which was formed at the same time, even constituting almost the whole of the mass, if the heat was not applied cautiously. After many experiments we succeeded in obtaining a satisfactory result by proceeding as follows. 13 gr. of tribromnitroresorcine diethylether were covered with absolute alcohol, and an alcoholic solution of sodic ethylate added. The flask containing the mixture was, after fitting it to a return condenser, immersed in a beaker of cold water, which was heated slowly. As the temperature rose the substance went into solution with a pale reddish color, and in a few minutes after that there was a sudden change, the solution becoming almost black, although the reaction was not at all violent. At this point the heating must be stopped to avoid the formation of a large quantity of the tarry impurity. The contents of the flask, which had a peculiar aromatic odor not belonging to the compound we have isolated, was allowed to evaporate to dryness spontaneously, and the residue washed several times with cold water, which was found to contain sodic bromide. The water left undissolved a most unpromising tarry mass with almost no sign of crystalline form, but by extracting it with hot ligroine a crystalline substance was obtained, which was purified by repeated crystallization from hot alcohol with the aid of bone-black until it melted constant at 115°, when it was dried at 100° and analyzed with the following results: —

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[*] Ber. d. ch. Ges., XX. 1554.

[†] Ann. Chem., CCLVII. 353.

[‡] Zeitschr. Physiol Chem., XV. 321.

[§] Ibid., XVI. 152.

I. 0.1897 gr. of the substance gave on combustion 0.2874 gr. of carbonic dioxide and 0.0782 gr. of water.

II. 0.1519 gr. of the substance gave according to the method of Carius 0.0985 gr. of argentic bromide.

	Calculated for $C_6H_2BrNO_2(OC_2H_5)_2$.	Found. I.	Found. II.
Carbon	41.38	41.31	
Hydrogen	4.14	4.58	
Bromine	27.58		27.60

The substance has therefore been formed from the tribromnitroresorcine diethylether by the replacement of two atoms of bromine by two of hydrogen, a reaction which is similar in principle to the replacement of the bromine by hydrogen in bromdinitroresorcine diethylether, when treated with a boiling solution of sodic ethylate in alcohol, and to the similar replacements of bromine by hydrogen in the formation of bromdinitrophenylmalonic ester and related substances from tribromdinitrobenzol and tribromtrinitrobenzol.

Properties of Bromnitroresorcine Diethylether, $C_6H_2BrNO_2(OC_2H_5)_2$.

The substance crystallizes from hot alcohol in long radiating silky white needles, which melt at 115°, and are soluble in cold alcohol, more freely in hot; freely soluble in cold methyl alcohol; very freely in benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroine, much more soluble in hot; essentially insoluble in water. Neither hydrochloric, nitric, nor sulphuric acid seems to have any action on it, and the same is the case with a solution of sodic hydrate.

XXII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF WATER UPON TRIBROMTRINITROBENZOL AND TRIBROMDINITROBENZOL.*

BY C. LORING JACKSON AND W. H. WARREN.

Presented June 15, 1892.

IN an article † recently published, C. A. Lobry de Bruyn describes the action of an aqueous solution of sodic carbonate upon the unsymmetrical trinitrobenzol (1, 2, 4) which produces the dinitrophenol (OH, 1, 2, 4) by the replacement of a nitro group by hydroxyl. After we had shown in an earlier paper ‡ that the nitro groups can be removed from tribromtrinitrobenzol by sodic alcoholates, M. Lobry de Bruyn suggested to us in the most courteous way that it would be interesting to see whether an aqueous solution of sodic carbonate would not have a similar effect on this substance, which seemed not improbable after his work already cited. The following paper contains an account of the work we undertook in accordance with this suggestion, the results of which can be briefly summarized as follows. Symmetrical tribromtrinitrobenzol (melting point 285°) is converted by boiling with sodic carbonate and water into a mixture of the sodium salts of trinitrophloroglucine and a tribromdinitrophenol, $C_6Br_3(NO_2)_2OH$, melting at 194°, which, so far as we can find, has not been described as yet. Tribromdinitrobenzol (melting point 192°, made from symmetrical tribrombenzol) gave under the same conditions a dibromdinitrophenol which melts at 147–148°, a melting point almost identical with that of the only other dibromdinitrophenol known (146°–146°.5), recently made by Garzino[*] by the action of nitric acid on the propionic ester of metabromphenol. This coincidence is, however, purely accidental, as in Garzino's phenol the bromine atoms stand in the ortho and para, in ours in the meta positions, to the hydroxyl. As was to be expected, the two phenols gave different salts, the potassium salt made by Garzino, containing one half of a molecule of water, while ours is anhydrous, his barium salt containing three, ours two molecules of water. Mixed with the dibromdinitrophenol is an oily phenol, which we have not succeeded in purifying in spite of many attempts.

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* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

† Rec. Trav. Chem., IX. 185.

‡ These Proceedings, XXV. 164.

The two substances, therefore, act with water and sodic carbonate in the same general manner as with sodic ethylate, the trinitro compound in both cases showing two parallel reactions, in one of which nitro groups, in the other bromine atoms, are removed, while the dinitro compound in both cases loses part of its bromine. It is to be observed, however, that while the alcoholate removes two nitro groups from the trinitro and two bromine atoms from the dinitro compound, water in each of these cases removes only one; although, like the alcoholates, it removes all three of the bromine atoms from the tribromtrinitrobenzol.

The constitution of the new tribromdinitrophenol can be only $C_6OHBrNO_2BrNO_2Br$, as the substance from which it is derived is symmetrical. The dibromdinitrophenol, on the other hand, can be either $C_6OHNO_2BrNO_2BrH$ or $C_6OHNO_2BrHBrNO_2$, and we have no experimental data for determining which of these two formulas is correct.

Action of Water and Sodic Carbonate on Tribromtrinitrobenzol.

As this action takes place very slowly it is better to carry it on as follows. Four or more flasks provided with return condensers were charged each with about 1 gr. of tribromtrinitrobenzol and a moderate quantity of a dilute solution of sodic carbonate, and allowed to boil for twelve or more hours. After a short time the solution turned yellow, and at the end of the boiling had become deep red. The unaltered tribromtrinitrobenzol was filtered out, and boiled again with a fresh solution of sodic carbonate. The deep red filtrate showed the presence of sodic bromide and sodic nitrite when the proper tests were applied. When acidified with dilute sulphuric acid it turned from red to yellow, and a white precipitate was thrown down, to which we first turned our attention.

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[*] Att. R. Acc. Sc. Torino, XXV. 263. Ber. d. ch. Ges., 1892, R. 119.

The white product of the reaction, which is insoluble in water, was purified by dissolving it in ammonic hydrate, precipitating the barium salt from this solution by means of baric chloride, and treating the precipitate with alcohol, in which the barium salt of this substance is soluble. The filtered alcoholic solution was evaporated to dryness, the residue recrystallized several times from hot water, and then converted back into the free phenol by treatment with dilute hydrochloric acid. The free phenol was next dissolved in as little hot alcohol as possible, diluted with water till a precipitate began to form, which was then redissolved by the addition of a drop or two of alcohol, when upon cooling the substance separated in good crystals. This rather long method of purification can be replaced by simple crystallization of the free phenol from alcohol and water in the way just described, but, if an absolutely pure product is needed, the whole method described above should be used. After it showed the constant melting point 194°, it was dried at 100° and analyzed with the following results: —

I. 0.1951 gr. of the substance gave 12 c.c. of nitrogen at a temperature of 23° and a pressure of 768.1 mm.

II. 0.2089 gr. of the substance gave according to the method of Carius 0.2787 gr. of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2OH$.	Found. I.	Found. II.
Nitrogen	6.65	7.00	
Bromine	57.01		56.76

These analyses show that the substance is a tribromdinitrophenol, and as it must have been formed from the tribromtrinitrobenzol by replacing one of the nitro groups by hydroxyl its constitution must be represented by the formula $C_6OHBrNO_2BrNO_2Br$. It is, so far as we are aware, the first tribromdinitrophenol which has been made.

To confirm the results of the preceding analyses the sodium salt was made by treating an excess of the phenol with pure sodic hydrate, filtering, and crystallizing from hot water, when it separated in long filiform yellow needles.

0.3076 gr. of this sodium salt gave 0.0504 gr. of sodic sulphate.

	Calculated for $C_6Br_3(NO_2)_2ONa$.	Found
Sodium	5.19	5.31

The sodium salt is soluble in ethyl or methyl alcohol even in the cold, and crystallizes from its alcoholic solution in long, flat, pointed needles.

Properties of Tribromdinitrophenol. — This substance crystallizes from dilute alcohol in square-ended needles usually grouped in arborescent or fan-shaped clusters looking like certain seaweeds; its color is white with a very faint shade of yellow. It melts at 194°, and is freely soluble in cold ethyl or methyl alcohol, or in ether, acetone, or glacial acetic acid ; somewhat less soluble in benzol or chloroform, although still freely soluble in these liquids; soluble in carbonic disulphide; slightly in ligroine; very slightly in cold water, somewhat more soluble in hot. Dilute alcohol is the best solvent for obtaining crystals. Its alcoholic solution is distinctly yellow. The three strong acids have no apparent action on it. With alkalies it forms colored salts. A solution of the sodium salt gave precipitates consisting of yellow needles with salts of zinc, nickel, manganese, cobalt, chromium, cadmium, or lead. Cupric salts gave light green needles. In order to characterize the substance still further, its barium salt was prepared and analyzed.

Baric Tribromdinitrophenylate, $[C_6Br_3(NO_2)_2O]_2Ba$.—This substance was made by adding baric chloride to a concentrated solution of the ammonium or sodium salt, collecting the precipitate, and recrystallizing it several times from hot water. The salt contained no water of crystallization.

I. 0.6621 gr. of the salt gave 0.1545 gr. of baric sulphate.
II. 0.5066 gr. of the salt gave 0.1182 gr. of baric sulphate.

	Calculated for $[C_6Br_3(NO_2)_2O]_2Ba$.	Found.	
		I.	II.
Barium	14.03	13.72	13.72

The baric tribromdinitrophenylate crystallizes from hot water in long yellow needles arranged in radiating circular groups. It is slightly soluble in cold water, more soluble in hot; freely in cold ethyl or methyl alcohol.

After the tribromdinitrophenol obtained by the acidification of the products of the reaction of water and sodic carbonate on tribrominitrobenzol had been filtered out, the filtrate was extracted with ether to obtain the organic substance, whose presence was indicated by its yellow color. The extract thus obtained melted over 190°, and contained bromine, indicating the probable presence of some tribromdinitrophenol. Upon boiling it with an aqueous solution of potassic carbonate, and allowing the solution to cool, small orange needles were obtained, which on acidification yielded the tribromdinitrophenol recognized by its crystalline form and melting point. The highly colored filtrate from these crystals was now treated with dilute sulphuric acid, extracted with ether, and the extract crystallized from water by slow evaporation, when the characteristic hexagonal prisms of trinitrophloroglucine were obtained. As they showed a somewhat low melting point, 163–164°, instead of 167°, (see the preceding paper,) the original substance and its barium salt were analyzed with the following results: —

0.2130 gr. of the substance gave 30.3 c.c. of nitrogen at a temperature of 19°.5 and a pressure of 776.1 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$	Found.
Nitrogen	16.09	16.67

0.7080 gr. of the barium salt gave 0.5409 gr. of baric sulphate.

	Calculated for $[C_6O_3(NO_2)_3]_2Ba_3$.	Found.
Barium	44.33	44.91

The barium salt contained no water of crystallization. These analyses leave no doubt that the substance is trinitrophloroglucine, and the behavior of tribromtrinitrobenzol with water is therefore represented by the following reactions: —

$$C_6Br_3(NO_2)_3 + 3\,H_2O = C_6(OH)_3(NO_2)_3 + 3\,HBr.$$
$$C_6Br_3(NO_2)_3 + H_2O = C_6Br_3(NO_2)_2OH + HNO_2.$$

The action of sodic hydrate and water upon tribromtrinitrobenzol was similar to that of sodic carbonate and water, the products being trinitrophloroglucine and tribromdinitrophenol. The action in this case takes place somewhat more quickly than with the carbonate, but we preferred to use sodic carbonate in order to avoid the action of the boiling hydrate upon the glass of the flask. In the cold, sodic hydrate seemed to have no action on tribromtrinitrobenzol, which surprised us because Lobry de Bruyn * has found that it acts in the cold on the unsymmetrical trinitrobenzol.

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* Rec. Trav. Chem., IX. 193.

Action of Tribromdinitrobenzol with Water and Sodic Carbonate.

Tribromdinitrobenzol (melting point 192°, made from symmetrical tribrombenzol) was boiled with an aqueous solution of sodic carbonate in the way just described for the trinitro compound. The action in this case was so slow that it was found better to continue the boiling for at least twenty-four hours before filtering. As in the preceding case, the color of the solution gradually became yellow, and later changed to red. After filtering out the unaltered tribromdinitrobenzol, the red filtrate, which contained sodic bromide and sodic nitrite, was acidified with dilute sulphuric acid, which turned it light yellow, and produced a cloudy precipitate, which after a long time collected on the bottom in the form of oil-drops. These were removed, the clear liquid extracted with ether, and the extract, which was small in amount and oily, added to the oil which had separated. This was then dissolved in ammonic hydrate and treated with baric chloride, when a precipitate was formed in a dark red solution.

The insoluble barium salt was decomposed with hydrochloric acid, and the phenol thus set free crystallized from dilute alcohol until it showed the constant melting point 147–148°, when it was dried at 100°, and analyzed with the following results: —

I. 0.1626 gr. of the substance gave by the method of Carius 0.1804 gr. of argentic bromide.

II. 0.2053 gr. of the substance gave 15.7 c.c. of nitrogen at a temperature of 26° and a pressure of 759.9 mm.

	Calculated for $C_6HBr_2OH(NO_2)_2$.	Found. I.	Found. II.
Bromine	46.78	47.22	
Nitrogen	8.19		8.49

These results prove that the substance is a dibromdinitrophenol formed by the replacement of one atom of bromine by one of hydroxyl, and as it is made from a symmetrical tribrom compound it must be isomeric with the one melting at 146°–146°.5 made by Garzino from metadibromphenol.

Properties of Dibromdinitrophenol. — This substance crystallizes from a hot alcoholic solution diluted with water until the substance begins to precipitate in thick yellow needles with square ends, arranged in radiating groups, although occasionally forms with two comb edges were observed. If crystallized from alcohol alone, in addition to the thick needles or prisms, other rather broad prismatic forms are observed, which have a notch in each end so that they resemble reels, or, when this formation is carried farther so that the notch has a flat bottom, crystals resembling spools are produced. Both these latter forms are very characteristic. It melts at 147–148°; and is very freely soluble in ethyl or methyl alcohol even in the cold, in ether, acetone, or glacial acetic acid; freely soluble in benzol or chloroform; soluble in carbonic disulphide; nearly insoluble in ligroine; water dissolves it to a certain extent when cold, still more, although not freely, when hot. The three strong acids have no apparent action on it. Alkalies form yellow salts with it.

Potassic Dibromdinitrophenylate, $C_6HBr_2OK(NO_2)_2$. — This salt was prepared by heating the free phenol with an aqueous solution of potassic carbonate, and was purified by crystallization from hot water. The salt was found to be free from water of crystallization. 0.1806 gr. of the air-dried salt lost only 0.0005 gr. at 120°. Garzino found one half of one molecule of water in his potassic dibromdinitrophenylate. The salt dried at 120° gave the following result on analysis: —

0.1664 gr. of the salt gave 0.0390 gr. of potassic sulphate.

	Calculated for $C_6HBr_2OK(NO_2)_2$	Found.
Potassium	10.29	10.52

The salt crystallizes from hot water in arborescent clusters of orange-yellow needles, which are somewhat soluble in alcohol, but not freely even when it is hot.

Baric Dibromdinitrophenylate, $[C_6HBr_2O(NO_2)_2]_2Ba2H_2O$. — The salt was made by boiling the phenol with water and baric carbonate, and purified by crystallization from boiling water, when it was analyzed with the following results: —

I. 0.2834 gr. of the salt dried in the air lost 0.0116 gr. at 120°.
II. 0.2834 gr. of the air-dried salt lost 0.0135 gr. at 120°.
III. 0.2831 gr. of the air-dried salt lost 0.0121 gr. at 120°.

	Calculated for $[C_6HBr_2O(NO_2)_2]_2Ba2H_2O$.	Found.		
		I	II	III.
Water	4.21	4.09	4.76	4.27

Three molecules of water of crystallization, the amount found by Garzino in his barium salt, would give 6.19 per cent of water.

IV. 0.3923 gr. of the salt dried at 120° gave 0.1112 gr. of baric sulphate.

V. 0.2668 gr. of the salt dried at 120° gave 0.0754 gr. of baric sulphate.

	Calculated for	Found.	
	$[C_6HBr_2O(NO_2)_2]_2Ba$.	IV.	V.
Barium	16.73	16.66	16.62

The salt is yellow while it contains its water of crystallization, but turns orange as it loses it, and this change takes place in a desiccator over sulphuric acid, as under these circumstances it loses all but an insignificant fraction of the water which it contains. The dried salt absorbs water very eagerly from the air, turning from orange to yellow again. It crystallizes from boiling water in clusters of radiating needles, and is soluble in alcohol.

The dark red filtrate from the precipitate of the barium salt of dibromdinitrophenol gave upon acidification an oily precipitate, which has resisted all our efforts to bring it into a state fit for analysis; it is probable that this could be done by often repeated fractional precipitation, but we do not think the identification of the substance of sufficient importance to justify the large expenditure of time and work necessary to provide material enough for this purpose. Several analyses, which we made to determine the purity of our preparations, seemed to point to the presence of a substance having the composition $C_6HBr_2NO_2(OH)_2$, but, as at the same time they proved that our products were decidedly impure, no weight should be given to this indication, although the formation of some such substance is to be expected from the appearance of sodic nitrite among the products of the reaction.

Sodic hydrate acts upon tribromdinitrobenzol in the same way that sodic carbonate does, but somewhat more rapidly. It has apparently no action in the cold.

PROCEEDINGS.

Eight hundred and forty-third Meeting.

May 26, 1891. — ANNUAL MEETING.

The PRESIDENT in the chair.

The death of D. Cecilio Pujazon, Director of the San Fernando Observatory, was announced; also, the death of Carl Wilhelm von Naegeli, of Munich, and of Carl Johann Maximowicz, of St. Petersburg, Foreign Honorary Members.

The Corresponding Secretary read the annual report of the Council.

The Treasurer and the Librarian presented their annual reports.

The following report was presented: —

Report of the Rumford Committee.

The Committee have held various meetings during the year with reference to the selection of a suitable candidate for the Rumford Medals. They respectfully submit that, in their opinion, the work of Professor E. C. Pickering on the photometry of the stars, and his work upon Stellar Spectra, fully justify the award to him of the Rumford Medals. By his invention of the meridian photometer he has succeeded in bringing order out of the chaos of photometric measurements hitherto made, by referring the photometric measures of all other stars to that of the Pole-star, and thus furnishing an estimate of the change of brightness of the stars with reference to the standard Pole-star. Estimates of the brightness of this star are also made, so that the photometry of the stars has been put upon a basis never before attained.

In his work upon the Draper memorial, Professor Pickering, adopting the method of Frauenhofer, and greatly enlarging the prisms and objectives employed by the latter, has succeeded in obtaining Stellar

Spectra which are comparable in size to the spectrum of the Sun as it was known to Frauenhofer. The method of the latter consisted in placing a prism of small refracting angle directly in front of the objective of the telescope, and in dispensing with the collimator. A cylindrical lens was employed to spread out the more or less linear spectra thus obtained. Frauenhofer's objective was about four inches in diameter, and the prism was a small one, suitable for this aperture. Professor Pickering employed a lens of eight inches in aperture, and a prism eight inches square, with a refracting angle of thirteen degrees. In some cases, three and four prisms were employed. The spectra were enlarged by means of a cylindrical lens, and also by giving the negative a motion in the direction of the lines upon the negative.

Professor Pickering has also employed spectrum analysis to the determination of the motions of the components of variable stars. He has discovered a large number of nebulæ and stars with singular spectra. A catalogue of stars with various types of spectra is now under way. The first volume of this catalogue has already been published. This work on stellar spectra is greatly in advance of anything else on this subject which has been done, and is worthy, in the opinion of the committee, of the award of the Rumford Medals.

For the Committee,
J. Lovering, *Chairman.*

This report was accepted by the Academy, and it was

Voted, That the Rumford Medal be awarded to Professor Edward C. Pickering.

On the motion of Professor Trowbridge, it was

Voted, To appropriate from the income of the Rumford Fund one hundred dollars ($100) to Professor E. H. Hall for an investigation of the conduction of heat in the walls of the cylinder of the steam-engine, and two hundred and fifty dollars ($250) to Professor B. O. Peirce for an investigation of the conduction of heat in the interior of solid bodies.

The following appropriations from the general fund were voted : —

For publications	$1,500
For the library	1,200
For the expenses of meetings . . .	200

On the motion of the Treasurer, it was

Voted, That the annual assessment for the ensuing year be five dollars.

The following gentlemen were elected members of the Academy: —

Henry Taber, of Worcester, to be a Resident Fellow in Class I., Section 1.

Henry Marion Howe, of Boston, to be a Resident Fellow in Class I., Section 3.

Louis Cabot, of Brookline, to be a Resident Fellow in Class II., Section 3.

Josiah Royce, of Cambridge, to be a Resident Fellow in Class III., Section 1.

Abner Cheney Goodell, Jr., of Salem, to be a Resident Fellow in Class III., Section 3.

Thomas Corwin Mendenhall, of Washington, to be an Associate Fellow in Class I., Section 2, in place of the late John H. C. Coffin.

George Park Fisher, of New Haven, to be an Associate Fellow in Class III., Section 3, in place of the late George Bancroft.

The annual election resulted in the choice of the following officers: —

JOSEPH LOVERING, *President.*
ANDREW P. PEABODY, *Vice-President.*
JOSIAH P. COOKE, *Corresponding Secretary.*
WILLIAM WATSON, *Recording Secretary.*
ELIOT C. CLARKE, *Treasurer.*
HENRY W. HAYNES, *Librarian.*

Council.

ARTHUR SEARLE, WILLIAM E. STORY, CHARLES R. CROSS,	of Class I.
SAMUEL H. SCUDDER, DAVID W. CHEEVER, SERENO WATSON,	of Class II.

Edward J. Lowell,
Martin Brimmer, } of Class III.
Lucien Carr,

Rumford Committee.

Wolcott Gibbs,	Joseph Lovering,
John Trowbridge,	George B Clark,
Josiah P. Cooke,	Erasmus D. Leavitt,

Benjamin O. Peirce.

Member of the Committee of Finance.

Augustus Lowell.

The President made appointments as follows: —

Committee of Publication.

Josiah P. Cooke, William G. Farlow,
John C. Ropes.

Committee on the Library.

Henry P. Bowditch, Amos E. Dolbear,
Edward J. Lowell.

Auditing Committee.

Henry G. Denny, Augustus Lowell.

The following papers were presented by title: —

On a Kephir-like Yeast found in the United States. By Charles L. Mix.

On the Matrical Equation $\phi\Omega = \Omega\phi$. By Henry Taber.

On the Movement of Electricity in Iron. By John Trowbridge and W. C. Sabine.

Eight hundred and forty-fourth Meeting.

June 10, 1891. — Monthly Meeting.

The President in the chair.

A biographical notice of Henry Jacob Bigelow, by Dr. Oliver W. Holmes, was read.

The following papers were presented by title: —

Notes on Fungi. By William G. Farlow.

Concerning the Life-History of Saccorhiza dermatodea (De la Pyl.) J. Ag. By William A. Setchell.

A Revision of the Atomic Weight of Copper. Fourth Paper. By Theodore W. Richards.

On some Considerations regarding Helmholtz's Theory of Consonance. By Charles R. Cross and Harry M. Goodwin.

On the Minimum Number of Vibrations necessary to determine Pitch. By Charles R. Cross and Margaret E. Maltby.

Eight hundred and forty-fifth Meeting.

October 14, 1891. — STATED MEETING.

The PRESIDENT in the chair.

The following letters were read by the Corresponding Secretary: from Louis Cabot, accepting Fellowship in the Academy; from the Tacoma Academy of Science, announcing its formation, and asking for the publications of the American Academy; from the Royal Academy of Sciences of Lisbon, announcing the death of its Secretary, José Maria Latino Coelho; from George Walter Hael, claiming that the clefts found upon the earth and the moon are due to the action of meteors; from the friends of Wilhelm Weber, announcing his death; from Eduard Marchal, announcing his election as Permanent Secretary of the Royal Academy of Belgium; from J. Veniezra, announcing his appointment as Director of the Marine Observatory of San Fernando; from the Royal Society of New South Wales, enclosing a programme of subjects for medals and money prizes to be obtained by competition; and from W. K. Warren, executor of the estate of Cyrus M. Warren, Fellow of the Academy, announcing a bequest to the Academy.

On motion of the Treasurer, the following vote was passed.

Whereas, The will of our late honored Associate, Cyrus M. Warren, contains the following provisions: —

"VII. I give and bequeath to the American Academy of Arts and Sciences of Boston one hundred shares of the capital stock of the Warren-Scharf Asphalt Paving Company, the proceeds, dividends, and income thereof to be applied by the said Academy, its trustees or directors, in their discretion, for the encouragement and advancement of research in the science or field of chemistry.

"VIII. I give and bequeath to said American Academy of Arts and Sciences fifty shares of the capital stock of the said Warren-Scharf Asphalt Paving Company, the proceeds thereof to be applied to or towards a building fund, for the purpose of erecting a building for the use of the library of said Academy, and for holding the meetings of said Academy; the same to be used in erecting such a structure when, in the opinion of the directors or trustees of said corporation, a sum sufficient shall be realized to justify such erection."

Voted, That the American Academy of Arts and Sciences accepts said bequests, and directs its Treasurer to keep the funds arising from them distinct, so that they may be applied in accordance with the conditions recited in the will.

The following gentlemen were elected members of the Academy: —

Warren Upham, of Somerville, to be a Resident Fellow in Class II., Section 1.

William Brewster, of Cambridge, to be a Resident Fellow in Class II., Section 3.

Edward Gardiner Gardiner, of Boston, to be a Resident Fellow in Class II., Section 3.

Samuel Jason Mixter, of Boston, to be a Resident Fellow in Class II., Section 4.

On motion of Dr. Williams, it was

Voted, To amend Standing Vote 10 by substituting "may" for "shall."

As amended, the standing vote reads as follows: —

"10. A meeting for receiving and discussing scientific communications may be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September."

Eight hundred and forty-sixth Meeting.

January 13, 1892. — STATED MEETING.

The Academy met at the house of the Hon. Martin Brimmer.

The VICE-PRESIDENT in the chair.

On the motion of the Recording Secretary, it was

Voted, To meet on adjournment on the second Wednesday in February next.

The chairman, in a brief address, announced that the Rumford Premium had been awarded to Professor Edward C. Pickering for his work on the photometry of the stars and upon stellar spectra.

Professor Pickering, in response, gave an account of the photographic work under his direction at the various stations in North and South America.

Dr. William Everett announced the death, on the 19th of December, 1891, of Sir George Biddell Airy, late Astronomer Royal, at Greenwich, elected a Foreign Honorary Member on the 25th of January, 1832, and since the death of Robert Treat Paine, in 1885, the senior member of the Academy.

Dr. William W. Jacques presented a paper entitled, "What Electricity is." This paper was illustrated by a new piece of apparatus invented by Dr. Jacques.

In the discussion which followed, Professor Cross, Judge Holmes, and Major Livermore participated.

Eight hundred and forty-seventh Meeting.

February 10, 1892. — ADJOURNED STATED MEETING.

The VICE-PRESIDENT in the chair.

The death on the 18th of January of Joseph Lovering, President of the Academy, was announced, and the meeting was devoted to a commemoration of his life and services.

The Vice-President, Rev. Andrew P. Peabody, opened the proceedings with the following words: —

We are convened this evening to express our sorrow for the death of our late President, and to offer our tribute to his memory. While it belongs to me officially to lead in the proceedings of the meeting, there is a certain fitness in my doing so, as my knowledge of Mr. Lovering antedated that of any one else here present. Most of you were his pupils; he was my pupil. In his Senior year in college his class recited in Astronomy to me. My only remembrance of him in the class-room is that he was one of the three or four on whom I relied to do credit to the class and their teacher in the oral examination at the end of the term. But he was brought into closer relation with me in another department. With three or four of his classmates he studied Hebrew with me for that entire year, and for that purpose spent three hours a week in my room. I then learned to admire the diligence, promptness, and accuracy which have marked his life-work ever since. He became, so far as was possible in a single year, a proficient in that language, which many who ought to be conversant with it find so hard to learn and so easy to forget.

Immediately after graduating he entered the Divinity School, and had nearly completed his preparation for the ministry when, in consequence of Professor Farrar's illness, he was requested to continue and complete a course of lectures in the department of Physics. Professor Farrar became a chronic invalid, and the place which Mr. Lovering first filled in an emergency he held, as Tutor and Professor, for fifty-three years. It was no small thing to succeed Professor Farrar. Those who heard his lectures, of whom few survive, were wont to speak of him as the most eloquent of men. Yet from the very first, both in Physics and in Astronomy, Mr. Lovering won a reputation that gave him a foremost rank as a scientific lecturer, which remained his when the grandchildren of his early classes sat under the wordfall still fresh and bright, because both old and ever new.

I speak here not only from abundant testimony, but from my own hearing. While the Lyceum was still an educational institution and enlisted the best men in its service, I had the pleasure of listening to several of his astronomical lectures, and at the same time of receiving him as my guest. I then could recognize at once the thoroughness of his scientific scholarship, his clearness of apprehension, his unsurpassed teaching power, and his gifts of style and manner, which could not but secure for him a marvellously strong hold on an intelligent audience.

Since my return to Cambridge I have been intimately associated with him, and these years have given me constant, and, were there room for growth, growing experience of traits of mind, heart, and character which have won my profound respect and sincere affection.

In the sixty years for which I have known him, there has been nothing in deed or word to break the record of a life pure, true, faithful, and kind. Rigidly conscientious in the least things as in the greatest, he has shown the worth and power of the religion whose worship and ordinances he has held in constant and sacred observance.

So young seemed he for his years, we looked not that he should be taken from us thus early. With bodily strength but slightly impaired, he retained his clearness, vigor, and activity of mind to the last. We are thankful that he passed away while we can feel his loss and mourn his departure, — that he was spared the prolonged decline and infirmity which we who are growing old most of all dread and deprecate. His life was beautifully rounded; its work done, and well done; and he was happy in the timeliness of his death no less than in the gratitude and honor which grew with his years, crowned his old age, and insure for him a precious and blessed memory.

With the approval of the Council, I offer for the Academy the following resolutions: —

Resolved, That, in the death of our late President, the Academy has lost a member whose reputation and whose many years of loyal service have contributed largely to its honor and prosperity, and a presiding officer whose assiduity, courtesy, and kindness have won for him from all his associates the most cordial and grateful regard.

Resolved, That we hold in precious remembrance his high scientific attainments, his eminent ability and success as a teacher, his place among the foremost in the reverence and love of the graduates of Harvard University, his pure and elevated character, and the worth of his example and influence as a Christian gentleman and scholar to the successive classes of students who, for more than half a century, passed under his instruction and discipline.

Resolved, That a copy of these resolutions be sent to his family, with the expression of our sincere sympathy with them in their bereavement.

The resolutions offered by the Vice-President were seconded by President Eliot of Harvard University: —

Professor Lovering's life seems to me to be better characterized by the word fidelity than by any other. He was just as faithful in the least things as in the greatest. Whatever work he undertook, he did thoroughly and steadily, although it might be uninteresting, mechanical, or really unsuitable for one of his station and powers. He heard recitations in Lardner's Natural Philosophy for many years of his life, and for a part of the time he heard each lesson three times over, — the class in Physics being divided into three sections. The book was very elementary, and far from interesting, and the class was boyish in attainments and in spirit; but year after year he performed that humble function with an absolute fidelity. For many years he gave illustrated lectures on all the main subjects in Physics, — generally two lectures a week throughout the academic year; and he himself made all the preparation for the experiments, with no assistance except that of the bell-ringer, who came in to help him move heavy pieces of apparatus or to work the air-pump. With perfect patience he performed weekly for years, without any assistant, this great amount of manual labor in connection with his lectures; and, as his lectures were repeated year after year during more than forty years, the weariness of repetition was added to the physical fatigue.

For twelve years, from 1857 to 1869, he was Regent of the College. That officer kept the records of absences and of the marks received by the students at their recitations. With his own hand Professor Lovering entered the absences and the marks in the record books, kept watch on the absences of every student in College, considered excuses, and reported delinquents to the Faculty week by week. The Regent exercised discretion and needed good judgment; but far the greater part of his time was devoted to accurate, patient, clerical labor. He was in his office three days of the week for two hours each day, and his compensation was five hundred dollars a year. I mention these details because they perfectly illustrate a quality in Professor Lovering which the men of a younger generation may well imitate, — a capacity for assiduous routine labor. Every great scholarly achievement is accomplished by just such faithful industry. An inspiration is a momentary flash; a high purpose has an instant of formation; but inspiration and purpose have to be wrought out through years of unremitting labor.

I have always admired in Professor Lovering the mixture of conservatism with openness of mind. His natural conservatism was modified by a true scientific candor. Change for its own sake he never desired; but he could be convinced by experience that a given change was an improvement. He held to the opinions and practices which he had adopted before he was forty years old; but his mind was also open to new projects. When the rapid expansion of Harvard University began in 1866, just after the close of the Civil War, Professor Lovering was already fifty-three years old and had been thirty years in the College service. When I was elected President he was fifty-six, — a time of life at which many men become impatient of changes which seriously affect their own habits of work. Yet Professor Lovering welcomed the project of moving the entire physical establishment from its narrow quarters in University Hall to larger rooms in Harvard Hall. He personally arranged the lower floor of Harvard Hall to receive the Department of Physics, and was highly content with the new accommodations of the department when the transfer was completed, in 1870. But the department grew apace, and the great gift of Mr. T. Jefferson Coolidge for the construction of a new physical laboratory made it possible to provide the department with larger quarters still, and opened the way to a great increase both of the teaching and of the investigation which it carried on. At the age of seventy-one Professor Lovering entered heartily into this large undertaking, brought to it a flexible and fertile mind, moved again from Harvard Hall to the Jefferson Physical Laboratory, and was glad to be appointed the first Director of that ample establishment.

He had been all his life an advocate of a single prescribed curriculum for Harvard College, whereby every student should pursue the same subjects; but after he was established as Director of the Jefferson Physical Laboratory, and had at his disposition an admirable lecture-room and a much enlarged cabinet of apparatus, I asked him one day if he would give some lectures to the Freshmen on general physics; for I wanted the Freshmen to have the advantage of his singular clearness of exposition. He asked if the Freshmen were not required to attend those lectures, — a question which then could only be answered in the affirmative. Whereupon he refused to give the lectures, saying that he would never again lecture in a required course, or to an audience whose attendance was required.

As I look back upon his life, it seems to me that it was to an extraordinary degree independent and self-contained. While entirely devoted to Harvard University as an institution, and inclined by temperament to support the constituted authorities of the University, he was nevertheless peculiarly independent in his own professorship, and had been ever since he was first elected to his chair, at the age of twenty-five. He served the College under seven Presidents, and I am sure that they all found him, as I did, considerate, firm but never factious in opposition, and loyal in support. His religious opinions were the quintessence of independence, and they were held with a firmness which no influence, however near and strong, could shake.

In the conduct of his household he would owe no man anything. Throughout a long life he was frugal and skilful in keeping his savings. His wants being simple, he thus earned the satisfaction of feeling during the last twenty years of his life that he was fairly independent in money matters, — a great satisfaction to a reserved and self-respecting man.

Faithful, constant, candid, independent, — these seem to me some of the high qualities of Joseph Lovering.

I ask leave, Mr. President, to second the resolutions you have offered.

After President Eliot, the Corresponding Secretary, Professor Josiah P. Cooke, addressed the Academy: —

I have been asked to speak of our late President as a teacher; and although I could wish that the duty had fallen to one who could portray more forcibly his remarkable ability as a college and public lecturer, I feel that there is a certain fitness in the assignment, since I have held intimate relations with him, first as pupil and afterwards as associate, for more than fifty years. My acquaintance with him began much earlier than his with me; for, when quite a youth, I was a constant attendant at his earlier lectures before the then recently established Lowell Institute, which were at that time given in the Odeon on Federal Street, near my father's home. From those lectures, continued several years in succession, I gained my earliest conceptions of Mechanics, Electricity, and Astronomy. I can remember many of the experimental illustrations as clearly as if the lectures had been given yesterday, and it is a striking evidence of the lecturer's definiteness of statement and aptness of illustration that a young boy should have been interested and instructed by lectures on subjects so abstruse. These lectures were given on Wednesday and Saturday afternoons, when there was a half holiday at school; and I remember they were well attended, although they were repetitions of lectures on the previous Tuesday and Friday evenings. At this time the elder Professor Silliman was charming the Lowell Institute audiences by his brilliant lectures on Chemistry, but Mr. Lovering did not suffer from the comparison; and if the fascination arising from the fluency and wealth of illustration of the elder man gave the bent to the boy's mind, he never questioned who was the more instructive lecturer.

At this time, from eight to ten years after his graduation from college and three to four years after his appointment as Hollis Professor at Cambridge, Mr. Lovering did not give me the impression of a young man, and through our long acquaintance he did not seem to age until within the few last years. Of course such an impression largely arises from the constancy of the mutual relations of men growing old together; but after making all allowance for the point of view, I think it will still appear that our colleague, although a very young old man, was a very old young man. As I look back I think this arose very much from the absence of that nervous susceptibility which is such a hindrance to most of us, and greatly increases the friction under which we work. Professor Lovering's imperturbability was notorious with all the graduates of the College during the last half-century. When he lectured he never showed the least emotion, and in the class-room his control of the muscles of his countenance was extraordinary. Not many years after the period I have mentioned, I passed through the regular course in Physics at our College, and I can see the Professor now, sitting like an inquisitor on an elevated chair overlooking the class, with his spectacles over the forehead, with the text-book, to which he never referred, on the desk before him, and directing his questions to one man after another in the clearest but most incisive terms, and in the exact order of the book, without hesitation or failure of memory. Each student was expected to take up the subject where the last left it, and I still wonder at the feats of memory which enabled some of the class to repeat mathematical formulas, even differential equations, without the remotest intelligent knowledge of their meaning. But although it was obvious that the Professor followed every detail and noticed every inaccuracy, yet the most absurd blunders and ridiculous incongruities never elicited a smile, or were any further noticed than by calling up the next man. No direct instruction, not even any elucidation of the book, was ever attempted. We did learn the book so far as it was intelligible to us, but nothing more. We must not, however, judge such exercises by our present standards. This formalism was the fashion in the education of the time, and the all but universal rule in the College.

The dulness of the recitations was, however, at times enlivened by the dry humor for which Professor Lovering was so noted among his friends. An incident which he was fond of telling himself is very characteristic, and recalls vividly those old college days. In the text of Herschel's Astronomy, which was recited verbatim for many years in the well known class-room at the south end of University Hall at Cambridge, there is quite a full description of the seven asteroids known at that time, and then follows a sentence something like this: "Besides these seven, others will probably be discovered." One day a faithful but formal student gave it, "Besides these, seven others will probably be discovered." The Professor, with his imperturbable fixed gaze, simply asked, "*Why seven?*" and called the next man. The bull was afterwards several times repeated, and the Professor had the credit of selecting his victims for the purpose; but I have also heard, what is more probable, that the class handed down the joke, and that the repetitions were the result of collusion among themselves.

The number of the asteroids now exceeds three hundred, and this astounding development of Herschel's prediction is only of a piece with what has passed in all departments of physical science. In the middle of the century the question between the undulatory theory of light and Newton's theory of emissions was still open, and in Brewster's Optics, the text-book we studied, the weight of authority was given to the latter theory. So also the different modes of energy were regarded as imponderable fluids, and a no inconsiderable part of the text-book on Electricity was taken up with a discussion of the merits of the then usually received theory of two electric fluids, as compared with Franklin's theory of one. During Mr. Lovering's long life the fundamental conceptions of physics entirely changed, and it was one of his great merits as a teacher that he kept abreast of the times, that he weighed systems impartially, and led his pupils to distinguish clearly between ascertained facts and the systems of science by which the facts are classified.

At the formal recitations I have described Mr. Lovering presided as an officer of the College to enforce a prescribed task. He did not consider that he was there to teach, in any proper sense of the term. He had assigned an excellent book from which it was our duty to learn, and from which we could learn, all of the subject we were expected to know, and it was solely his duty to see that we did our work. This does not seem to us now a very high ideal of a college exercise, although doubtless the lazy men and the dullards did gain an occasional idea from hearing their classmates' recitations. Still, it must be remembered that this was the attitude of teachers in almost all the class-room exercises of the period, and no one could have done the duty assigned to him more faithfully or more impartially than Mr. Lovering.

But if Professor Lovering, with most college teachers of his time, did not feel it incumbent on him to give personal instruction in his recitations, it was very different with his stated lectures. At these he displayed his full intellectual strength, and I look back on them as in many respects the most profitable part of my college course. He was one of the best lecturers I have ever known, and I have known the greatest masters of my time. He may not have had the imagination of Faraday or the grace of Dumas, but his lectures were instructive in the highest degree. The chief sources of his power are not far to seek. In the first place, he had the great art of bringing his reasoning and his illustrations to the intellectual level of his hearers, without belittling his subject. He was a popular lecturer in the very best sense. He did not commit the common error of seeking to gain attention through trivialities, or of attempting to appear learned by using technical terms; but he sought to raise his audience from their lower plane to his level, and he succeeded to a wonderful extent. Again, he had remarkable clearness of statement, and he gained this in the only way it can be gained, by seeking definiteness of conception. He did not trust to the inspiration of the moment to make a difficulty, however familiar to him, intelligible to others; but he laboriously studied every subject he taught until he had a firm grasp of all the concepts, and then the stream was clear because the spring was clear. Lastly, Mr. Lovering had to a greater degree than I have ever known, the power of looking at physical problems from different sides, and seeing them in all their aspects. This gave him great fertility in illustration, and often enabled him to present a subject from a point of view wholly unexpected even by adepts in the science.

We often say in the laboratory, when troubled by the failures of a faithful student, but unskilful experimenter, that a chemist, like a poet, is born, not made, and the same must be equally true of a physicist; and if we consider only the power of original investigation, there is doubtless much truth in this trite apothegm; but it is not true of many great scientific scholars and teachers, and of this Mr. Lovering's success is a conspicuous example. In college he was one of the first scholars of his class, but although a good mathematician his tastes were linguistic and literary rather than scientific, and he had already entered on the study of Divinity when a chance opening determined his career in life. The opinion has often been expressed that the intuitions and enthusiasm of an original investigator are necessary to make a great scientific teacher, and if by this is meant necessary to direct to the best advantage the studies of those born to the purple, I should agree in the judgment. But, on the other hand, the devious and narrow paths through which the investigator is constantly led in the chase of natural phenomena are apt to give him a very limited view, while the scholar who commands a larger field is better able to point out to ordinary minds the extent and bearings of the numerous details which it has required very many explorers to bring to light. This was strikingly true of Mr. Lovering. He was not, as he himself would be the first to avow, a born investigator, although, as his successor will doubtless tell you, he did very substantial work as an original student; but he was a great teacher, and I am persuaded that the experiences of his education to which I have referred had an important influence on the result. He came to the study of physics as a ripe literary scholar; and he dwelt on its various fields, with their intricate relations, until he had acquired clear conceptions of the whole ground, and it was thus that he gained the power of presenting all the details with such clearness and force.

So called "original research" is now a fad in education, and we are in danger of overlooking the fact that the scholar and teacher is no less important to the community than the investigator. It is absurd to contend which is the more important member of the body politic. No one has pressed on this community more persistently than myself the importance of scientific investigation, not primarily for the results it may yield, but chiefly as a great influence towards sustaining the higher life of the nation, and yet I feel assured that the explorers would soon lose their reckoning were not there also a class of scholars to co-ordinate their results and supervise their work. It is easy to sneer at popular lectures, and I have as great a contempt as any one for mere glitter and froth; but the lecturer who can raise men to a higher intellectual level confers a benefit on the community which is none the less real because its effects may not be at once apparent.

Faraday was one of the very few men who was at the same time a great teacher and a great investigator. I never was more impressed by any intellectual achievement than by the popular, even juvenile, lectures which I once had the privilege of attending at the Royal Institution in London. And, however great the bequests of knowledge this investigator left to mankind, I greatly doubt whether, when the final account is closed, the greatest contribution of Faraday to human welfare will not be found to be his popular lectures. It has been well said that the greatest discovery of Sir Humphry Davy was Faraday, — a mere bookbinder's apprentice when he was fascinated by Davy's brilliant lectures, — and who can number the intellectual offspring of the still greater teacher? It is the misfortune of a college teacher that the successive classes pass on long before the fruits of his influence have time to mature; but the influence lives, and could we trace the effects of our associate's work I am sure that we should be satisfied that fifty years of devoted service has not been spent in vain.

A substantial part of Professor Lovering's work as a teacher, which we must not forget, are the numerous popular essays on scientific subjects which he published from time to time in various periodicals. Several of the earlier of these appeared in the "American Almanac," and most of the later in the Proceedings of this Academy, including addresses on the presentation of the Rumford Medal, and biographical notices printed in connection with the Reports of the Council. What is probably a complete list, as it was revised by Professor Lovering himself, may be found in the "Popular Science Monthly" for September, 1889, in connection with a short biographical notice. In these essays, popular only in that they do not assume a specialist's knowledge, are preserved to us the striking characteristics of Professor Lovering's teaching to which I have referred. They are as fresh to-day as when written, and are not only highly interesting as choice examples of popular scientific exposition, but also of permanent value, as exhibiting in a striking manner the changes in the modes of scientific thought during the last half-century. I am anxious that the most suitable of these essays for the purpose should be collected and reproduced in a handsome volume, and in my judgment this would be the most fitting memorial we could prepare of our late honored President.

Professor John Trowbridge, the successor of Professor Lovering as Director of the Jefferson Physical Laboratory in Harvard University, next spoke: —

In due time Professor Lovering's scientific labors will receive attention in a more elaborate way than I can pretend to devote to them to-night. His death is so recent that the time for the critical summing up of the labors of a long life has not been sufficient for a careful presentation to you of the subjects in which he worked. and upon which his reputation as a scientific man will rest. The subjects of Astronomy, Meteorology, Magnetism, and Optics were favorite ones with him. I find in the American Journal of Science a paper on Meteoric Observations made at Cambridge in 1839. This paper marks, I believe, the beginning of his scientific work, and following it were a large number of articles on the subjects I have mentioned. The catalogue of scientific papers published by the Royal Society of England contains between the years 1839 and 1863 the titles of eighteen papers. Among these are the following: —

On Magnetic Observations made at Harvard University. Memoirs Am. Acad., 1846.
On Coronæ and Halos. Proc. Am. Acad., 1848.
On the American Prime Meridian. American Journal of Science, 1850.
New Experiments and Modes of illustrating the Laws of Light and Sound. Proc. Am. Acad., 1852.
On Motions of Rotation. Proc. Am. Acad., 1852.
On Donati's Comet. Proc. Am. Acad., 1857.
Memoir upon the Secular Periodicity of the Aurora Borealis. Proc. Am. Acad., 1857.
On the Velocity of Light and the Sun's Distance. Proc. Am. Acad., 1862.

This number of papers can be greatly increased by the addition of his scientific essays and addresses. He also did much routine scientific work in connection with the determination of longitude by the Coast Survey, holding a position as Astronomer to the Survey during the administration of Professor Benjamin Peirce.

The subjects of sound and light, and wave motion in general, I have said, were favorite ones with him, and he took great pleasure in adding to the Physical Cabinet apparatus to illustrate these subjects; so that to-day they form the most complete portion of the apparatus for demonstration which he left to his successors. I remember that he once showed me an apparatus which he had devised for obtaining the velocity of electricity, which combined in an ingenious manner the apparatus in sound with which he was so familiar and certain arrangements of electro-magnets. It is doubtful whether Professor Lovering's contemporaries, who occupied chairs of Natural Philosophy in American colleges can show so large an amount of scientific work as he performed in addition to his college exercises.

After listening to such appreciative words as we have heard from those who have been the life-long friends of Professor Lovering, I feel that my testimonial may seem scant. Those who attended his lectures have a store of remembrances of his wise sayings, of his peculiar humor, which often threw the light of a different philosophy from that which he was professedly elucidating, and which showed that literary tendency which made him capable of giving wise counsel over a wide range of University matters. Strange to say I never heard one of his college lectures, but I knew from conversations with him that he could present a subject with a certain finish and fine deliberation which was the despair of new beginners in the art of demonstration. I have seen him prepare an experiment for a lecture with that patience which Balzac is said to have devoted to his paragraphs, taking every possible care that the form in which the idea was to be presented should not break down through that spirit of total depravity which sometimes seems to preside over physical experimentation. Professor Lovering, imbued with a philosophy of life which I am inclined to believe was one of his most remarkable attributes, knew full well that this depravity of inanimate objects was the expression of want of patience and thought in the experimenter, and he never hesitated to try an experiment scores of times before its presentation at the lecture table.

All who enjoyed intimate friendship with him must have felt the strength of this fine deliberation and careful conduct toward the forces which shape our physical life. Acting with him on the Rumford Committee, and sometimes on other committees, I have felt that in voting with him I should be safely conservative, and the wisdom which only a long life of great thought can give was apparent in every deliberation.

Professor Lovering belonged to a school of Professors of Physics which is very different from that which is now prevailing in our universities and technical schools; for the laboratory method of instruction is taking the place of the lecture method. It was hinted that he hesitated to change the method which had been a life one with him. I doubt, moreover, whether any one who had reached the age even of fifty, and had never accustomed himself to laboratory work, would be willing to enter upon the arduous and trying work of physical research. This work must be undertaken chiefly by younger men. One could always take one's results to Professor Lovering and have them illuminated by the stores of his knowledge of the history of the subject. Professor Eustis once remarked to me, that I should find Professor Lovering a very sound man in his subject, and I verified this remark frequently. I have spoken of the humor with which he often threw the light of philosophy upon things animate and inanimate. A very egotistical student was once giving his views to us at a seaside resort, and after his departure Professor Lovering remarked that he was "all-sufficient, self-sufficient, and insufficient."

In the course of a lecture he was contrasting the undulatory theory of light with the corpuscular theory, and after stating with a certain judicial manner the objections to the latter theory and leaving it no ground to stand on, he finished it thus, in his slow, deliberative tones: "The reason that the corpuscular theory is no longer advocated is that all its advocates are dead."

Some men are compelled to assert themselves through the whole course of their lives, for the world is not vividly conscious of their presence in it. Professor Lovering, however, had a marked personality, which did not seem to require self-assertion. He was a marked man in any gathering. Perhaps he gave the impression that he had conquered the world and could smile at its foibles, and one desired to catch the secret of his self-possession, with the expectation of having it told with humor. It seems to me that he resembled certain great philosophers, and might be said to be a follower of Aristotle.

We all remember that his presentation of a subject had a certain old-time stateliness of manner, which was perfect in the days when oratory was much esteemed, and had not become affected by an age of telegrams and telephone communications. I believe that a collection of the essays of Professor Lovering on physical and astronomical subjects would show that discriminating spirit and deliberative wisdom, and that peculiar literary style, which characterized him, and which must leave a permanent remembrance upon the minds of all who knew him.

Still further tributes to the noble character and great worth of our deceased President were made in the following letters.

From Hon. Robert C. Winthrop.

My dear Dr. Peabody, — I regret extremely that age and infirmities will prevent my attending the meeting of the Academy to-morrow evening. It would afford me peculiar satisfaction to be present at the commemoration of our lamented friend, Professor Lovering, and to listen to the tributes proposed for the occasion. His services as President of the Academy constitute but a small part of his claim to consideration. His lifelong loyalty to the cause of science, and his devotion to the University as Professor for more than half a century, entitle him to a most grateful remembrance.

Nor can I forget my association with him, for several years past, as one of the Trustees of the Peabody Museum of American Archæology and Ethnology.

I say nothing of the pleasant relations which I enjoyed with him as a friend, and of the respect which I have always entertained for his character.

Believe me, with renewed regrets that I cannot attend the meeting,

Yours, sincerely,

Robert C. Winthrop.

From Professor W. W. Goodwin, of Harvard University.

My dear Dr. Peabody, — I am very sorry that I cannot attend the meeting of the Academy this evening in memory of Professor Lovering. Of our late President as a man of science I have no right to speak, for I can claim only to be one of the large class of his admirers who viewed his scientific attainments from a respectful distance. But I have known him for more than forty years as a kind friend, and in later years as a genial companion; and by his death I have lost one for whom I felt deep respect and warm affection.

I first knew Mr. Lovering as lecturer and teacher in Harvard College. In 1849, when I first came under his instruction, he was in his best vigor, and his lectures on mechanics, optics, electricity, and magnetism always seemed to me perfect of their kind, and admirably adapted to their purpose, which was to give a general knowledge of physical science to a whole college class, who had no opportunity to study in detail more than a small fraction of the sciences which his lectures covered. It seems to lie beyond the province of our reformed College to give this general view of the physical sciences, or indeed of any of the sciences, to our students; and perhaps we do not always remember that the knowledge which every student had an opportunity to gain from Mr. Lovering's lectures ought still to be brought within the reach of every one at some stage of his education.

In the old College Faculty, as I first knew it in 1856, Professor Lovering was one of the most important and influential members. He was constant in his attendance, and he always had a decided opinion on every question that came up. He often decided a long and wandering debate which had led to nothing, by a few words of plain common sense, or even by a humorous remark into which an argument was condensed. His dry humor was second only to that with which that master of humor, President James Walker, constantly entertained and often convinced the College Faculty. During a great part of the presidencies of Mr. Sparks, Dr. Walker, Mr. Felton, and Dr. Hill, he held the post of Regent, which has since been extended into the less regal but more responsible one of Dean. A comparison of the Regent's office in Mr. Lovering's day, open four hours *a week*, with the present Dean's office, open nine hours *a day*, shows the growth of the College, and also the changed relation of the students to the officers of administration. In all the affairs of his office, Mr. Lovering was exact and systematic to the last degree. His fixed principles of college government, and his wonderful memory of facts, names, and faces, enabled him to be perfectly consistent in all his dealings with students, and his high standard of justice made it almost certain that no one could be wronged by his decisions. He was, indeed, a model executive officer, and his long administration as Regent did much to establish and confirm the policy of Harvard College for a period of twenty years.

I well remember one of the first occasions when one of the speakers at a College exhibition uttered strong and decided anti-slavery sentiments. One of the older Professors remonstrated to Mr. Lovering, and expressed his surprise that such a passage should have been allowed to be spoken. Mr. Lovering replied, "I have heard the other side of that question here all my life; and I think it is quite time that we heard this side now."

Mr. Lovering's sense of fairness was one of his most marked characteristics. He was also a man of remarkable kindness and sympathy, which often took the form of most efficient action even when he seemed to try to repress its expression in words. His whole personality was, indeed, a most striking one, which impressed every one who met him, while it was fully appreciated only by those who knew him best.

Regretting that I cannot listen to the tributes of respect which will be offered to his memory this evening, I remain ever

Yours, sincerely,

W. W. Goodwin.

From Mr. Justin Winsor, Librarian of Harvard University.

My dear Dr. Peabody, — Mr. Lovering's failure to be present at a gathering of the Thursday Evening Club in Boston was so unprecedented, that at the meeting which was held during his last illness everybody remarked upon his absence, and it was the first intimation most of us had that he was confined to his house. A fortnight before, at its previous meeting, I had talked with him about his constancy of attendance, and he told me that he had never missed a meeting, and he was among the older members of the Club. Even to the last he was ready to contribute his share to the edification of its members, and he said to me on this last meeting of his attendance, that he was ready to be called upon for a paper, if there should at any time be a gap to be filled.

His enjoyment of the Club was in accordance with such a record of unrivalled faithfulness. He was alive to every phase of intellectual progress, and he found the surprises and novelties offered to the club in such direction, often in advance of more public enunciation, stimulating and enjoyable. He took much gratification in the prompt response which was found among the members of this Club, as well as among the officers and friends of the University, when a testimonial was prepared for him on his retirement from the active duties of his professorship. This movement resulted in a dinner given to him in Boston, which was presided over by the President of the University. Mr. Lovering made a response to the principal toast, in which, with his peculiar humor, he reverted to the events of his long career as a teacher. Dr. Holmes referred to the extent of this career as only comparable in the history of the College to that of Tutor Flynt, and suggested that a duplicate of that old preceptor's silver teapot, which had come down to him by family lines, should make part of the testimonial to Mr. Lovering. This reproduction was carefully made, and Mr. Lovering a little later placed it among his household treasures with evident satisfaction. He was also asked to sit for his portrait, and no sitter could ever have been more faithful to the demands of the artist than he was, — prompt in his place and never tiring. The picture which represents him in his gown as a Professor, sitting full face, was placed in the parlor of his house, ultimately to be transferred to the walls of Memorial Hall.

Yours, sincerely,

JUSTIN WINSOR.

From Professor F. W. Putnam, of the Peabody Museum of American Archæology and Ethnology.

MY DEAR DR. PEABODY, — On the day assigned for the memorial meeting of the Academy in honor of its late President, Professor Joseph Lovering, I was unexpectedly called out of town, and was thus prevented from uniting with the other members in offering tributes to his memory. Will you therefore permit me to express my appreciation of one whom for over thirty years it has been my privilege to count as a friend.

At the time of my entering the Scientific School, in 1856, Professor Lovering was in the prime of life, and it was my good fortune to attend his lectures. For eight years following, I often had the pleasure of meeting him, and ever found him genial and ready to give freely of his store of knowledge to an inquiring student.

In 1868-69, we were again intimately associated on the occasion of his trip to Europe, when he delegated to me his position as Permanent Secretary of the American Association for the Advancement of Science, and the editorship of the Chicago and Salem volumes of Proceedings. Again, in 1872, when he was elected President of the Association and resigned the office of Permanent Secretary, it fell to my lot to succeed him in the Secretaryship.

This election to the Presidency was not only a unanimous offering of the Association to a distinguished member, but also a merited recognition of his long and faithful service as its trusted executive officer.

Professor Lovering was the second Permanent Secretary of the Association, and was elected in 1854 as the successor to Professor Baird. He filled the position for nineteen years, and it is well known by the older members that his efforts were unceasing in fostering the objects of the Association. He fully believed in the benefits which would accrue to American science from these annual gatherings of scientific men in different parts of the country. In conversation on this subject, he always expressed his firm belief in the important work of the Association, and the advantage to be derived from this united effort to encourage and develop scientific work by interesting hundreds of cultured men and women in scientific objects, and by stimulating isolated workers to greater exertion. Eminently social and agreeable, he always took great pleasure in these gatherings of kindred spirits, and was an almost constant attendant at the meetings until the last few years of his life. His advice in the Council meetings of the Association, while always somewhat conservative, was nevertheless favorable to progress. His remarks were always earnest, but never hasty or passionate, and were so sure to carry conviction that his views of a subject generally prevailed.

For the third time we were brought into intimate official relations when as President of the Academy, in 1888, Professor Lovering became a Trustee of the Peabody Museum of American Archæology and Ethnology of Harvard University, as the successor of the late Professor Asa Gray. In this office he was always prompt in attendance at the meetings of the Board and often visited the Museum, in which he was greatly interested.

While Professor Lovering was always serious in his work, and when speaking upon important subjects, yet no one liked better than he the moderate pleasures of life, or enjoyed sociability with a greater zest.

Thus it has been my fortune to know this friend under many conditions, and through all these years and varied circumstances, official and social, I have never found him lacking in sympathy and readiness to advise and assist in every way in his power, and there has never been a ripple of antagonism to mar our friendship.

Although we deeply regret the loss of this dear friend from our midst, it will always be a pleasure to cherish the memory of his many virtues, his true friendship, his love for his fellow men, and his devotion to science.

Yours, sincerely,

F. W. PUTNAM.

The resolutions were unanimously adopted by the large company of Resident Fellows in attendance at the meeting.

Andrew Howland Russell, of Boston, was elected a Resident Fellow in Class I., Section 4.

Eight hundred and forty-eighth Meeting.

March 9, 1892. — STATED MEETING.

The VICE-PRESIDENT in the chair.

The Corresponding Secretary read letters announcing the death of Sir William Macleay, of Sydney; of John Couch Adams, of Cambridge, England, Foreign Honorary Member; and of the Grand Duke Constantin Nicolayevitch, President of the Imperial Russian Geographical Society. Letters were received from Samuel J. Mixter and Warren Upham, accepting Fellowship in the Academy.

The Vice-President announced the death of Henry Ingersoll Bowditch, George Bassett Clark, Thomas Sterry Hunt, William Raymond Lee, and Sereno Watson, Resident Fellows; and of George Washington Cullum and Noah Porter, Associate Fellows.

On motion of the Corresponding Secretary, it was

Voted, To meet on adjournment on the 13th of April.

On motion of the Recording Secretary, it was

Voted, To amend Standing Vote 9 by substituting "eight" for "half-past seven," so as to read: —

"9. The annual meeting and the other stated meetings shall be holden at eight o'clock, P. M."

The vacancy occasioned by the death of the President, Joseph Lovering, was filled by the election of

JOSIAH P. COOKE, *President.*

Dr. Peabody, in relinquishing the chair, expressed the pleasure he had experienced while serving as an officer of the Academy, and intimated his intention of declining re-election as Vice-President at the approaching annual meeting.

The President elect addressed the Academy as follows: —

I thank you most warmly for the very great honor you have conferred by this election as your President, and I need not to assure you that I shall work for the best interests of our Academy so long as your favor and my health and strength permit. I have been for nearly forty years a member, and for thirty-eight years I have discharged the duties of one or another of your subordinate offices. For nineteen years I have been your Corresponding Secretary, and during that time have edited twenty volumes of your Proceedings and Memoirs, — much more than one half of all the material published by the Academy since its foundation. You can understand from this what pleasure it will give me to finish this long period of service as your presiding officer. Moreover, my associations with the Academy go back before my membership.

It so happened that my honored father occupied for a long period a law office at No. 9 State Street, adjoining that of John Pickering, that noble man and learned scholar, who was your President from 1839 to 1846. Through the kindness of this great man, who warmly encouraged a boy's scientific tastes, I had free access to his library and the use of his books; and it was there that I came to know that there was such a learned society as the American Academy of Arts and Sciences, and to indulge the thought that I might one day make myself worthy to become a member of such an illustrious body. I cannot but confess that the lustre has become somewhat dimmed with use; but my colleagues will appreciate how great a privilege I feel it is to fill the place once held by this beloved patron of my youth, and later by Jacob Bigelow, the good physician of my boyhood, and by Asa Gray and by Joseph Lovering, my college teachers and the warm friends of my manhood.

The PRESIDENT in the chair.

Dr. Seth C. Chandler presented a paper entitled, "Results of Researches on Variable Stars." A discussion of this paper followed, and remarks were made by Messrs. Searle, Edmands, and Dolbear.

Dr. Henry Taber presented a paper entitled, "On a Theorem of Sylvester's relating to Degenerate Matrices."

Eight hundred and forty-ninth Meeting.

April 13, 1892. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

The President read a letter from Captain Andrew H. Russell, accepting Fellowship in the Academy; also, a circular from the Executive Committee of the Congress of Engineers and Architects at Palermo, inviting members of the Academy to take part in its deliberations.

The vacancies in the Rumford Committee, occasioned by the death of Joseph Lovering and of George B. Clark, were filled by the election of the following

Members of the Rumford Committee:

EDWARD C. PICKERING, CHARLES R. CROSS.

Dr. Seth C. Chandler presented a paper entitled, "Results of Researches on Variations of Latitudes."

Professor Jackson presented, by title, a paper on the Formation of the Anhydrides of Benzoic and substituted Benzoic Acids. By George D. Moore and Daniel F. O'Regan.

Eight hundred and fiftieth Meeting.

May 11, 1892. — SOCIAL MEETING.

The Academy met at the University Museum, Cambridge.

The PRESIDENT in the chair.

The President announced the death of August Wilhelm Hofmann, of Berlin, Foreign Honorary Member of the Academy, and gave a brief sketch of his scientific work.

The following papers were read: —

Biographical Memoir of the late Sereno Watson. By George L. Goodale.

On Bivalent Carbon. By John U. Nef.

Diamonds in Meteoric Iron. By Oliver W. Huntington.

The mineral cabinet of Harvard College was fortunate enough to obtain, through the liberality of Francis Bartlett, Esq., one of the two original masses of meteoric iron, weighing 154 pounds, brought by Dr. A. E. Foote from near Cañon Diablo, Arizona. As this iron had been said to contain diamond, the following experiments were made with a view of isolating if possible the diamondiferous material. A mass of about one hundred grams' weight was dissolved in acid assisted by a battery.

The iron was supported on a perforated platinum cone hung in a platinum bowl filled with acid, and the cone was made the positive pole and the dish the negative pole of a Bunsen cell. When the iron had disappeared, there was left on the cone a large amount of a black slime. This was repeatedly washed and the heavier particles collected. This residue examined under a microscope showed black and white particles, the black particles being mainly soft amorphous carbon, while the composition of the white particles appeared less easy to determine, though when rubbed over a watch-glass certain grains readily scratched the surface.

The material was then digested over a steam bath for many hours with strong hydrofluoric acid, and some of the white particles disappeared, showing them to have been silicious. Most of them, however, resisted the action of the acid. These last were carefully separated by hand, and appeared to the eye like a quantity of fine white beach sand, and under the microscope they were transparent and of a brilliant lustre. A single particle was then mounted in a point of metallic lead, and when drawn across a watch-crystal it gave out the familiar singing noise so characteristic of a glass-cutter's tool, and with the same result, namely, of actually cutting the glass completely through. To verify the phenomenon, successive particles were used for the purpose, and with the same result. The experiment was then tried on a topaz, and the same little mineral point was found to scratch topaz almost as readily as it did glass. It was finally applied to a polished sapphire, and readily scratched that also, proving beyond question that this residue of small, white, transparent grains must be diamond, though no well formed crystals could be recognized.

Dr. Huntington then exhibited in the hollow of a watch-glass the diamonds which he had obtained from the meteorite.

Catalogue of the Magnitudes of Southern Stars from 0° to –30° declination, to the Magnitude of 7.0 inclusive. By Edwin F. Sawyer.

AMERICAN ACADEMY OF ARTS AND SCIENCES.

Report of the Council. — Presented May 24, 1892.

BIOGRAPHICAL NOTICES.

Edward Burgess	By Alpheus Hyatt.
George Bassett Clark	Arthur Searle.
William Prescott Dexter	W. T. Russell.
Thomas Sterry Hunt	William O. Crosby.
Joseph Lovering	Josiah P. Cooke.
George Hinckley Lyman	Henry W. Williams.
David Humphreys Storer	Samuel H. Scudder.
Cyrus Moors Warren	Francis H. Storer.
Sereno Watson	George L. Goodale.
George Washington Cullum	William R. Livermore.
John C. Fremont	George S. Boutwell.
Thomas Hill	Andrew P. Peabody.
Joseph Leidy	Thomas George Lee.
Noah Porter	Andrew P. Peabody.
John Couch Adams	Arthur Searle.
George Biddell Airy	Arthur Searle.
Wilhelm Eduard Weber	Amos E. Dolbear.

Notices of Bowditch, Lee, Lowell, Barker, Ferrel, Rutherfurd, Caligny, Hofmann, and Ramsay are necessarily deferred to the next volume; while those of Dexter, Fremont, and Leidy, deferred from last year, are given below.

REPORT OF THE COUNCIL.

Since the Annual Meeting of the 26th of May, 1891, the Academy has lost by death twenty-three members ; — eleven Fellows, Henry Ingersoll Bowditch, Edward Burgess, George Bassett Clark, Thomas Sterry Hunt, William Raymond Lee, Joseph Lovering, James Russell Lowell, George Hinckley Lyman, David Humphreys Storer, Cyrus Moors Warren, and Sereno Watson; six Associate Fellows, Fordyce Barker, George Washington Cullum, William Ferrel, Thomas Hill, Noah Porter, and Lewis Morris Rutherfurd; and six Foreign Honorary Members, John Couch Adams, Sir George B. Airy, Anatole François Hüe Marquis de Caligny, August Wilhelm Hofmann, Sir Andrew Crombie Ramsay, and Wilhelm Eduard Weber.

RESIDENT FELLOWS.

EDWARD BURGESS.

Edward Burgess was born, June 30, 1848, at West Sandwich, Mass., and graduated at Harvard in the class of 1871. During his college life he studied natural history successfully, and was extremely fond of yachting, showing in this way the forcible working of the two dominating tastes that he afterwards carried to successful issues when it became important to follow them out with practical assiduity. He became Secretary and Librarian of the Boston Society of Natural History by election on February 21, 1872, and continued to hold these offices until May 2, 1888, when he resigned to devote himself wholly to the profession of a naval architect. He died at Boston, July 12, 1891.

His scientific work never engrossed his whole attention, as did the study of the best construction of sailing vessels, but his work was of the highest excellence in certain directions, commanding the respectful attention of men of the first rank in all parts of the world.

Samuel H. Scudder, the eminent entomologist, speaks in his obituary notice of Burgess with such authority that we have done little besides follow him in this brief article.

Soon after his connection with the Society of Natural History began, he commenced to work in collaboration with Mr. Scudder upon the abdominal appendages of New England butterflies, the results of which were published in Scudder's celebrated volumes on those animals. This was followed by a joint work published by these two authors upon the similar organs of the different species in the Thanaos. He subsequently published a series of anatomical papers beginning with an investigation of the structure of the head and of the mouth parts in the Psocidæ. The most important and valuable was that upon the anatomy of the Milkweed Butterfly. Mr. Scudder says of this: " In the text and plates accompanying the larger memoir he gave a more precise and detailed account of both the external and internal anatomy of the insect discussed than had ever been given before of the anatomy of any perfect butterfly, and brought to light a number of interesting points that had been nearly or quite overlooked before, such as the nature of the striæ on the scales, the musculature of the tongue and its intimate structure, the cuticular processes of the food reservoir, the backward course and chambered enlargement of the aorta within the thorax, and the false claspers of the male abdomen, a remarkable series of new observations to have been made upon a single insect."

His discovery of the strange course of the aorta in this butterfly led him to pursue the subject further by the dissection of a number of lepidopterous insects, and to embody its results in a brief illustrated paper in the Proceedings of the Boston Society of Natural History in the following year, by which he showed " that, if we except the peculiar course of the anterior branch (of the aorta) in the hawk-moth, we have (in the Lepidoptera) a gradual series from the butterflies downward. In the former a distinct horizontal aortal chamber is present; in the higher moths a vertical node replaces the chamber, and this vanishes in the lower moths."

His discovery of the curious locked up mouth of the larva of Dysticus in an animal previously supposed to have been mouthless followed this in the same year, and his anatomy of the grasshopper, Anabrus, and of the moth, Aletia, followed each other in succession, and all of them were executed with such skill in every respect as to command the attention of entomologists in every part of the world.

He was considered an authority upon the Diptera, and his collection of these animals contained fourteen thousand specimens. He however published but little, although he had really done a large amount of systematic work upon this order.

His favorite recreation in the summer time was yachting ; and while engaged in this apparently aimless occupation, he was really studying the construction and handling of vessels, and following out a natural bent leading to the development of the best and highest qualities of his mind.

The services he rendered to natural history, although of high excellence, were not unique, whereas it may be said with confidence that his work in naval architecture was a reform of the first magnitude. Constructors worked empirically and were not able to produce improvements in any two consecutive boats which would show the certain working out of results by means of a scientific method. Burgess applied the discipline his mind had gained from the study of science to the problem of boat building, and demonstrated the fact that a system could be invented and used which would give certain results.

Knowing Mr. Burgess personally, and occupying for many years the same office with him, also having some acquaintance with the subject and its difficulties, it amazed me to see the modest confidence he possessed in his own application of scientific methods to this problem. His replies to my questions, on two successive occasions following the first victory in the international races, invariably disclaimed any great merit on his own part, or any certainty that he could construct a better model than his rivals, and he was fond of ending the argument by a highly characteristic remark, — " A scientific method and experience ought to enable me to beat myself."

The spirit of the scientist was dominant in him, and even during times of the highest excitement I never knew him to admit that he desired his boat would win in the international races. He always insisted that he hoped the best model would win, declaring that the object to be attained was the highest excellence in naval construction, and this was to him more important than any other. It is a matter of serious regret to his friends, and perhaps a great loss to the world, that he never reached the goal of his desires, — an opportunity to apply his methods and test their value on a large scale in the construction of first-class steamers.

Personally, Edward Burgess endeared himself to all closely associated with him by his uniform good nature and fairness. He never plumed himself in the slightest degree upon his successes, and the public adulation which crowned him after the international races was received with gratification, but did not in the least disturb his equability or increase his self-esteem. His untimely death was a national loss, for there is no doubt among those that knew him that he was capable of *steady progressive development*, a quality of body and mind which, in combination with genius, gave strong assurance of a future greater even than the past.

GEORGE BASSETT CLARK.

George Bassett Clark was born in Lowell, Mass., on February 14, 1827. His early education was received at the Grammar School, the High School, and afterwards at Mr. Whitman's private school in Cambridge, to which place his father had removed in 1835. In 1844, the subject of this notice entered Phillips Academy at Andover, where he completed his literary education, and began for himself an original course of practical training in the work which was subsequently to distinguish him. He had already shown an interest in the mechanical arts, and had made his proficiency with the lathe a source of some little profit to himself, by manufacturing toys for his juvenile accquaintances. He now procured a piece of an old bell, which he took home with him, and from which he undertook to construct the speculum of a reflecting telescope. Undeterred by the doubts of his elders as to the possibility of bringing his scheme to a successful conclusion, he presently gave them a practical proof of his ability by producing an instrument with which a satisfactory view of Jupiter and its satellites could be obtained. This first success encouraged him to attempt the construction of refracting as well as of reflecting telescopes; and his father, becoming interested in his son's experiments, was thus led to join him in the work. Neither the father nor the son, however, seems at this time to have expected seriously to undertake the business of an optician. Mr. Alvan Clark continued to employ himself as a portrait-painter, while the younger man, after finishing his course at the Phillips Academy, engaged in the work of civil engineering, and was employed in that capacity upon the Boston and Maine and the Ogdensburg and Lake Champlain Railroads.

The discovery of gold in California, in 1848, turned his attention to still another industry, and he was among the first who hastened to the new land of promise. His fortune differed little from that of the greater number of his fellow emigrants, and, after several months of adventure and hardship, he returned, richer in experience than in worldly goods. In his journey to California, he crossed the Isthmus of Panama in the manner then customary, by a boat voyage up the Chagres River and by difficult paths across the hills beyond. On one occasion, his guides, whose language he could not speak, armed him and themselves with clubs, and set out with him upon an expedition the purpose of which he could not conjecture. It appeared that their object was peaceable, being only to obtain a supply of provisions in the way of legitimate trade, but that the clubs were necessary to defend the party against the dogs who had to be encountered before the trading could begin. In California itself provisions were still more difficult to obtain, and when obtained were of the worst quality; moreover, the first part of the return voyage was attended by many depressing circumstances. The excitement of travel and adventure was probably overbalanced in Mr. Clark's mind by the painful impression made upon his kindly nature by the scenes which he had witnessed, for in after life he appeared to dislike recalling the incidents of his expedition.

Upon his return, he resumed the work which had most interested him in his boyhood, and opened a shop in East Cambridge for making and repairing instruments. He was soon joined in this business by his father and by his younger brother, although his father still kept his Boston studio open for several years. Mr. George B. Clark's personal history from this time is in great measure that of the firm of Alvan Clark and Sons, which he had been so largely instrumental in founding. The business was continued in East Cambridge until 1860, when it was removed to the situation in Cambridgeport where it is still conducted.

While Mr. George B. Clark was thoroughly familiar with the purely optical portion of the work undertaken by the firm, the part of that work which ordinarily depended chiefly upon him was that of providing the mountings of telescopes, and of planning and making the metallic parts of scientific apparatus of various kinds. In this work he was highly ingenious, and his ingenuity was, if possible, surpassed by his perseverance. He was frequently called upon to contrive means for the execution of new plans which had occurred to men of science, and he could not be defeated by the mechanical difficulties, which were often great, in the way of the desired result, when he had once assured himself that the principles involved in the plans were correct. With a mere verbal description, or at most a rough sketch, of the instrument required, he would readily undertake the solution of the frequently perplexing problems which presented themselves when its actual construction was begun. When it was finished, he was equally indefatigable in experimenting with it, not only before it left the workshop, but after it had been delivered to the purchaser, until it had been brought into such condition as fully to answer its purpose. He was indifferent to the mere external appearance of his work, but spared no pains to make the results to be obtained with it as perfect as possible.

Upon the criterion laid down by Solomon, few men have ever been as well qualified as Mr. Clark to stand before kings; for he was pre-eminently a man diligent in his business. This virtue, no doubt, had the corresponding defect, that he was almost incapable of allowing himself reasonable time for rest and recreation. The holidays of his workmen were usually spent by him in solitary labor, directed to testing and improving the instruments in course of construction, or in consultation with some scientific customer upon the best means of evading the difficulties which were hindering the execution of some new plan. When an important order was in the hands of the firm, he could not rest till the work was accomplished. Thus, when the instruments for the national observations of the transit of Venus in 1874 were to be constructed, and, owing to delay in the receipt of definite orders the time for their execution was very limited, Mr. Clark labored so unremittingly to accomplish what was required that as soon as the instruments were sent off he was prostrated by illness, from the effects of which, it is apprehended, he never fully recovered. Still, notwithstanding weariness and imperfect health, the remainder of his life exhibited the same continuous industry which had previously marked it. During this period, the equipment of the Observatory of Harvard College was largely increased. Numbers of new instruments applicable to new forms of observation were called for from the firm of Alvan Clark and Sons; and Mr. George B. Clark devoted to supplying these needs, not merely the attention due to a customer, but the interest of a friend. Such men will always be overworked, for their willingness and ability naturally overwhelm them with calls for their assistance.

To enumerate the important instruments in the construction of which Mr. Clark took part would be merely to give a list of the celebrated telescopes and other pieces of apparatus which have been furnished during the last forty years by the firm of Alvan Clark and Sons. But attention may be called particularly to those instruments in which ingenuity of metallic construction was especially necessary; for this, as has been said, was the province in which Mr. George B. Clark's abilities were most marked. When the gearing required in the apparatus for determining the velocity of light, constructed for Professor Newcomb, proved to be soon worn out by the rapidity of revolution required, Mr. Clark succeeded in applying the necessary remedy by introducing raw hide into a certain part of the apparatus, instead of metal. Among the instruments made for Harvard College Observatory and other institutions of Cambridge and Boston, in the construction of which his skill and zeal were peculiarly advantageous, may be mentioned several large spectroscopes, photometers, and photographic instruments.

The singularly genial and kindly temperament which Mr. Clark inherited from his beloved father insured him cordial regard, and even affectionate sympathy, among a wider circle than that of his immediate relatives and associates. His face and manner bore a stamp of refinement of feeling which would not have been expected in a man whose education and whose occupations were of so exclusively practical a character. His incessant devotion to his business left him no leisure for those pursuits which are traditionally regarded as tending to promote gentleness as well as gentility; but nature had supplied him in this respect with more merit than most men can acquire by training.

He was married in 1857 to Miss J. M. Mosely, who survives him; but he left no children. Although the failure of his health had for several years been evident, his death by apoplexy on December 20, 1891, found him still busy with his work. His memory will be cherished by all who knew him, and the instruments which he planned will long testify to his skill by the scientific results which they furnish.

WILLIAM PRESCOTT DEXTER.

William Prescott Dexter was the son of Franklin Dexter and of Elizabeth, daughter of Judge William Prescott. He came of distinguished ancestry. His great-grandfather on the mother's side commanded the American troops at Bunker Hill. The historian William Hickling Prescott was his uncle. His grandfather, Samuel Dexter, was an eminent statesman. Both his grandfathers were members of this Academy, and they held high rank as lawyers, as did his father also. All of them were prominent citizens. So too was his distant kinsman, Aaron Dexter, M.D., likewise a member of this Academy, who held the Chair of Chemistry and Materia Medica in Harvard College from 1783 to 1816, and was thenceforth Professor Emeritus until his death in 1829.

When thirteen years old, William P. Dexter passed from the Boston Latin School to Harvard College, and was graduated thence in 1838, and from the Harvard Medical School in 1842. He established himself as a practising physician, first in Boston and then in Brookline, and devoted himself to this profession during a number of years. In 1847 he married Margaret Austin, daughter of William Austin, lawyer and essayist, always to be remembered in American literature as the author of " Peter Rugg, the Missing Man."

The following sketch of Dexter's after life has been furnished by his friend, Dr. William J. Russell, of London.

William Prescott Dexter was born at Boston, on the 10th of December, 1820. He studied medicine at Harvard College, and graduated in 1838. After leaving college, he practised medicine at Brookline for a few years, but his strong interest in pure science and his longing to devote himself solely to scientific pursuits made him feel the irksomeness of the ordinary routine of a medical practitioner's life, and induced him to give up the medical profession, and to go abroad in order to study chemistry. From this time to the end of his life he devoted himself entirely to the prosecution of that science. His interest in and devotion to chemistry never flagged, and although he did not reside permanently in any one place, but lived in different parts of Germany, in England, and occasionally returned to America for a short time, still his one great interest in life was the study of chemistry, and wherever he settled for any length of time he always had a laboratory. Few there are who have devoted their lives so entirely to science simply for its own sake. No desire for place or for emolument stimulated Dexter's love for chemistry; it was a pure desire to increase knowledge and to learn with rigorous accuracy the true nature of the phenomena he was interested in. In organic chemistry he took comparatively little interest; the theoretical conceptions which play so important a part in this branch of chemistry he was loath to admit, and he did not sufficiently believe in them to be interested by them; but it was in inorganic chemistry, and especially in the analytical branch of the science, that his whole interest was centred. Rose's Analytical Chemistry was ever a book of fascinating interest to him. He studied it when in America, when he had little or no means of carrying out its precepts, and it was this book which induced him to give up his professional career and go to Germany, and it was to

Rose's laboratory in Berlin that he first went. Even before leaving America, and while still in practice, he revised and published in 1850, in a separate form, the tables for the calculation of analyses which were appended to Rose's work. This entailed a very considerable amount of labor; for the tables were most thoroughly revised, and nothing but the most perfect accuracy would satisfy him; and he tells us in the Preface, that "every calculation was performed by myself both by direct division and by the use of logarithms." Also extraordinary care seems to have been taken to avoid all errors of the press.

After working for some length of time in Berlin, Dexter went to Göttingen and worked in Wöhler's laboratory, and from Göttingen he went to Heidelberg. Here he worked for about twelve months in Professor Bunsen's laboratory, and it was during this time that he carried out his most important published work, his determination of the atomic weight of antimony, which was published in 1857. This work was admirably carried out. The writer well remembers the care and thought bestowed upon it, how every possible error he could conceive of was considered and eliminated, and the wonderful accuracy with which the manipulation was performed. The method first tried was the simple one of precipitating the antimony by gold; but this method was found to give inaccurate results, and was abandoned, and the direct oxidation of the metal substituted. Other chemists were working on the same subject at this time, two of them, Dumas and Kessler, obtaining results very nearly agreeing with Dexter's number, 122.34; but Schneider obtained the number 120.3. These researches led to the adoption at that time of the number 122.0. Since then further researches have been made. Cooke in 1880 published a very elaborate and thorough investigation of the matter. Other investigators and other distinct methods have confirmed the lower number, and 120 is now generally adopted as the true atomic weight of antimony. At the same time, it is difficult to see where the error, if there be one, crept into Dexter's experiments. All the papers which Dexter published related to analytical chemistry, some appearing in Poggendorf's Annalen, and some in the Proceedings of the American Academy and in the American Journal of Science. His interest and his special ability lay in analytical chemistry. He was one of the most perfect manipulators who have ever lived; the precision and accuracy with which he performed the different processes of analysis were astonishing. Every step was thought out, and then performed as carefully and intelligently as possible. Of late years the discovery of a perfect method, and consequently one of general application, for the estimation of phosphoric acid, engrossed entirely Dexter's attention, and for many years he was considering and experimenting on this subject. The subject had an extraordinary fascination for him. No difficulties, and he met with many, could daunt him, and he has left behind much work of a very interesting and high kind on this subject. At last he seems to have discovered a method which would satisfy even his exacting requirements, but unfortunately he did not live to complete his work. The introduction to it he had worked out, in the form of a most rigorous examination of the methods now in use, and the degree of accuracy of which they are susceptible, but the completion of his method remains unfinished. During the last few years of his life he settled in Leamington, England, and led there a peaceful life, making the best room of his house into a laboratory, and devoting himself to the study of analytical chemistry, and amusing himself with some practical problems in higher mathematics. He died on the 8th of November, 1890.

Papers by William Prescott Dexter.

1. Renal Calculus. Passage through the Ureter, assisted by the Use of Ether. Boston Medical and Surgical Journal, 1849, XL. 219.
2. Tabulæ Atomicæ: The Chemical Tables for the Calculation of Quantitative Analyses of H. Rose. Recalculated for the more recent Determinations of Atomic Weights, and with other Alterations and Additions, by William P. Dexter. Boston, 1850, 8vo, pp. 70.
3. Ueber die Trennung der Thonerde vom Chromoxyd. Poggendorf's Annalen, 1853, LXXXIX. 142.
4. Ueber die Trennung der Wolframsaeure vom Zinnoxyd. Poggendorf's Annalen, 1854, XCII. 335.
5. [Analysis of Polyhalit.] Reported by H. Rose, Bericht der Akademie der Wissenschaft zu Berlin. 1854, p. 412.
6. Ueber das Atomgewicht des Antimons. Poggendorf's Annalen, 1857, C. 563.
7. On the Double Salts of Cyanide of Mercury. Proceedings of the American Academy, V. 355. (9 Dec., 1861.)
8. Remarks upon the recent Determinations of the Atomic Weight of Antimony. Proc. Amer. Acad., V. 359. (14 Jan., 1862.)
9. On the Aluminates of Baryta. Proc. Amer. Acad., VI. 97. (28 Jan., 1863.)
10. Obituary Notice of Heinrich Rose. Proc. Amer. Acad., 24 May, 1864, VI. 312.
11. On the Preparation of Hydrofluoric Acid. American Journal of Science, 1866, [2.], XLII. 110.

12. New Chemical Apparatus. American Journal of Science, 1868, [2.], XLVI. 51.
13. On the Sulphates of Oxide of Antimony. American Journal of Science, 1868, [2.], XLVI. 78.
14. Obituary Notice of Dr. Augustus Matthiessen. American Journal of Science, 1871, [3.], I. 73.

THOMAS STERRY HUNT.

THE subject of this notice, whose death occurred in New York City, February 12, 1892, made extensive contributions to American science, and has permanently identified his name with its progress and development. Choosing two of the most rapidly advancing sciences, chemistry and geology, as his field of work, and studying these especially in their intimate and extensive interactions, he had a large and honorable share in giving form to our present knowledge upon these subjects. Although an indefatigable experimenter and an extensive observer, Dr. Hunt was also eminently an original and philosophic thinker, and took an influential part in the establishment of the most matured scientific theories.

Thomas Sterry Hunt was born in Norwich, Conn., on September 5, 1826. His ancestor, William Hunt, was one of the founders of Concord, Mass., in 1635. His maternal grandfather, Consider Sterry, of Norwich, was a civil engineer and mathematician, and was the author of text-books of arithmetic and algebra published one hundred years ago.

While the subject of this sketch was a child, the family moved to Poughkeepsie on the Hudson. There the father died when Thomas, the oldest son, was twelve; and the mother returned with her family of six young children to the old home in Connecticut. For a short time Thomas attended the public school; but it was for a short time only, as he thus early was required to share the burden of the family support, and to seek employment.

At that time his intention was to study medicine. Under the counter of the store in which he was employed he kept a skeleton, as well as his home-made chemical apparatus. Two local physicians assisted the brilliant boy, thus educating himself, by the loan of books.

In 1845 he went to New Haven during the meeting of the Association of Naturalists and Geologists, and obtained work as a reporter on a New York paper. But a more important issue of this trip was a visit to the elder Silliman, whom the boy had met in Norwich after one of the Professor's lectures. Struck by his precocious proficiency in chemistry and mineralogy, Professor Silliman facilitated his admission to Yale College. Erelong he became paid assistant to Professor Silliman, Jr., who was then making an extended series of water analyses, in which Hunt aided him, and was admitted a member of his household. The struggle for a livelihood had ceased.

While at Yale, between his eighteenth and twentieth years, he contributed eighteen papers to Silliman's Journal, and wrote the Organic Chemistry for Silliman's First Principles. In the Preface to the first edition, published in December, 1846, Professor Silliman acknowledged the aid rendered by his young colleague as follows: "The author takes pleasure in acknowledging the important aid derived in this portion of the work from his friend and professional assistant, Mr. Thomas S. Hunt, whose familiarity with the philosophy and details of chemistry will not fail to make him one of its ablest followers."

In 1847, while preparing to continue his studies in Great Britain, he was appointed to a position on the Geological Survey of Vermont, under Professor C. B. Adams, but soon resigned to accept a similar position on the Canadian Survey. In February, 1847, he entered on his duties as Chemist and Mineralogist to the Geological Survey of Canada, taking possession of that small study and still smaller bedroom opening off the Laboratory in St. Gabriel Street, Montreal, where for so many years he, without any laboratory assistant, not only did the routine analytical work of the Survey, but made many experimental investigations in chemical geology. His literary activity was prodigious, as evinced not only by the scope but by the number of his contributions, no fewer than seventy-six articles appearing under his name in the Second Series of Silliman's Journal alone. It was at this time that he conceived and published those wide views on chemical and general geology which were embodied in the greater works of his later years. His strictly official work as Chemist and Mineralogist would have been more than enough for most men; but he supplemented it by spending several months of each year in the field, and by assisting his chief, Sir William Logan, in the literary and administrative work of the Survey. Every year from 1856 to 1862 he spent the spring months in Quebec, lecturing on chemistry in the French language before Laval University; and for four years he filled the Chair of Applied Chemistry and Mineralogy in McGill University, at Montreal. In 1872 he resigned his position on the Geological Survey of Canada, after a service of twenty-five years, to accept the Chair of Geology at the Massachusetts Institute of Technology, which he held until 1878.

His eminence in science was early recognized by his election, in 1859, as a Fellow of the Royal Society of London, where for some years he enjoyed the distinction of being the youngest Fellow. Early in his career Harvard conferred on him the degree of M. A., and Laval that of LL. D.; and in 1881 the University of Cambridge, England, also honored him with the degree of LL. D. The names of home and foreign societies which enrolled him on their honor lists would fill a page. He was a member of the National Academy of Science; was Acting President in 1871 of the American Association for the Advancement of Science; and President in 1877 of the American Institute of Mining Engineers. He was the first President by election of the Royal Society of Canada, and held office at every meeting of the International Geological Congress which his health permitted him to attend. His influence at these important conferences was heightened by his perfect familiarity with the French language.

What he considered his most important contributions to science up to 1886, he embodied in two volumes, "Chemical and Geological Essays" (1874), and "Mineral Physiology and Physiography" (1886). His mature views on the nature and effects of Chemism he published in 1887, under the title of "A New Basis for Chemistry"; and he applied the same principles to Mineralogy in his latest work, "Systematic Mineralogy" (1891), based on a natural classification.

From this incomplete sketch of his tireless and many-sided activity we can form some idea of his learning and of his industry. He never knew what it was to be idle, and never wasted his power on irrelevant and desultory work, and thus he became the master of many sciences. He was a good mathematician. Although not himself a profound physicist, he was able to appreciate the more recondite results of modern physical investigations. He felt very keenly those ineffable affinities which bind every energy in nature to one central force, and had a lofty conception of the interdependence of the laws of the universe, and of the harmonious blending therefor of chemistry and physics.

As a geologist, Hunt's original work, whether in the field or in the laboratory, was done among the crystalline rocks. He received his geological training from the Director of the Canadian Survey, Sir William E. Logan; and his text-books were the Azoic rocks to the north of the Lakes and the St. Lawrence, and the Palæozoic rocks of southeastern Quebec. To the knowledge of the stratigraphy thus gained he added, from his store of chemical and mineralogical knowledge and from his laboratory investigations, the facts and hypothetical deductions which appeared to him to give as conclusive probabilities to the life study of those older barren strata as the evolution of vegetable and animal organisms gives to the history of later rocks. He combined in his intellectual equipment the practical experience of a field geologist with a theoretic erudition in geology and allied science such as few of his fellow workers could claim to possess. He was therefore warranted, as the area of his geological view grew, in shifting his ground on certain subordinate points. The most notable instance of such a change of position was that taken in his Presidential address before the American Association for the Advancement of Science, in 1871, when he subdivided the crystalline rocks which had been previously classed as Laurentian and Huronian into six groups, and altered the stratigraphic relations of what was known in the Canadian Survey as the Quebec Group. Whether the subject was important enough to warrant the vehemence with which he maintained his ground and sustained his argument may, perhaps, be doubted; but to Hunt truth was truth, and the relative proportion and importance of the truth had no weight with him.

It is not on his work as a stratigraphical geologist that Dr. Hunt's fame will mainly rest; but on his achievements in lithology and chemistry, and on the broad generalizations which he drew as to the early development of the earth. There are essays in his second series, elaborating the crenitic theory, which rise to a high pitch of eloquence, and which any one of literary tastes, though utterly ignorant of science, will read with rapt enjoyment. Last year, after completing his "Systematic Mineralogy," and when so feeble that he could only move from his bed to his desk, he commenced a book entitled "The History of an Earth," in which it was his purpose to expand, in a connected treatise, his splendid generalizations on stellar and telluric chemistry, and especially to trace the influence of water under heat and pressure in decomposing the primitive basic crust of the earth, and in creating out of the primary elements the older crystalline rocks, and again in re-creating from their sterile ashes, through decay and death, the newer life-supporting and life-entombing strata which contain, written in generation after generation, the newer history of the earth. But death frustrated this and other literary projects.

Chemistry was Hunt's first love, and he never deserted her. When he studied geology, his impulse was to seek below the visible results of mechanical causes for the all-pervading chemical forces and agencies which, by dissociation and combination, by integration and disintegration of elemental matter throughout all space, are building up other worlds, as they built up ours. In his system of mineralogy neither outward resemblances, nor similarity of crystalline structure, nor possession of common elements, but the relation of hardness to condensation, and the further relation of these qualities to chemical indifference, constituted the basis for his classification of mineral species. Whether amidst such a multitude of individual species he, in his first arrangement, assigned to each its proper place, may well be doubted, without questioning the substantial correctness of the principle on which his chemical and natural-historical classification rests. Yet it is impossible to follow, in his "Systematic Mineralogy," the beautiful progressive series of quotients deduced from the formula $V = p \div d$ (V being the coefficient of condensation, p the chemical equivalent, and d the specific gravity), as calculated for the species under each genus, without being convinced that Hunt heard and expressed one of those wonderful harmonies of which it is granted to but few mortals to catch the theme, amid the complexity and often apparent discord of nature's contending voices.

The doctrine of the equivalency of volumes, as applicable to liquid and solid species, as well as to the gases, on which is founded Hunt's "Natural System of Mineralogy," had dawned on his mind very early in his chemical studies; but its larger significance was revealed to him only toward the close of his life. To him the domain of chemistry was much wider than it had been held to be under the old conventional theory, which drew such precise lines between chemical and mechanical forces. Like most philosophical chemists of to-day, he regarded all solution as chemical union, and all chemical union as nothing else than solution. In his view all precipitation and all crystallization from solutions involve chemical change, and all chemical species may theoretically exist in a dissolved state, from which they pass into polymeric mineral species, often insoluble. Regarding the same substance in its different polymeric states, due to different degrees of condensation, as representing so many different chemical and mineral species, he, like other chemists, was driven to construct chemical formulas much more complex than those which satisfied the requirements of the Daltonian atomic theory as it had been previously understood.

This New Basis of Chemistry was to Hunt no longer theory, but fact. He had believed for many years that the solid and liquid mineral species known to us are formed by processes of intrinsic condensation, or so called polymerization, from simple chemical species. He knew, with every chemist, that the determination of the coefficient of condensation is a problem of the highest moment, — a problem which had been neglected in the belief that it did not admit of solution. When, therefore, in 1886, he reached what he regarded as a solution of this insoluble problem, and propounded the theorem that "the volume, not only of gases and vapors, but of all species, whether gaseous, liquid, or solid, is constant, and that the integral weight varies directly as the density," he rejoiced in the conviction that he had realized and expressed one of the great laws of nature, after which he had been groping all his life.

While throughout all his maturer years he pondered over the deeper problems of pure science, he was also actively engaged in practical pursuits. The papers he has written on technical subjects would fill wellnigh as many volumes as his theoretical and purely scientific memoirs.

It is proper to state that this notice has been, in the main, compiled from those which have appeared elsewhere, and especially from the extended biographical sketch read by Mr. James Douglas before the American Institute of Mining Engineers last June, and published in the current volume (XX.) of the Transactions of the Institute.

JOSEPH LOVERING.

Professor Lovering was born to humble circumstances at Charlestown, Massachusetts, December 25, 1813, and received his early education in the public schools of that place. His father, a subordinate town officer, was a member of the Harvard Church, then under the pastoral care of the Rev. Dr. James Walker, subsequently Professor in Harvard College and its President. At the public school, young Lovering had proved himself an apt and bright scholar, and this circumstance led to his employment by Dr. Walker as a reader. The prophetic judgment of this wise man, whom Harvard students so soon after learned to respect and honor, recognized in the lad unusual promise, and he not only encouraged him to prepare for college, but also aided him with personal instruction and advanced the money necessary to pay his college expenses, a loan which he was soon able to repay. In 1830 Lovering entered the Sophomore Class at Harvard, and was graduated in due course in 1833. He was a distinguished scholar, standing fourth in a class which furnished six Professors to the Alma Mater and four to other institutions. At the Commencement he delivered the Latin Salutatory Oration, and three years later, when his class were entitled to receive the Master's degree, he delivered the Valedictory Oration, according to the custom of that day.

During the first year after his graduation, Mr. Lovering taught a small private school in Charlestown. In the autumn of 1834 he entered the Divinity School in Cambridge, and remained there two years. During a part of the academical year 1834–35 he assisted Professor Peirce in the instruction of the College classes in mathematics. In 1835-36 he was Proctor and Instructor in mathematics, and during a part of the year he conducted the morning and evening services in the College Chapel in place of the regularly officiating clergyman. In 1836–37 he was Tutor in Mathematics and Lecturer in Natural Philosophy, taking the work of Professor Farrar, whose failing health had led him to resign, and in 1838 he definitely succeeded Professor Farrar as Hollis Professor of Mathematics and Natural Philosophy. The active duties of this office Professor Lovering discharged without assistance for the unprecedented term of fifty years and on resigning in 1888 he was appointed by the Corporation of the University Hollis Professor Emeritus, and thus continued his connection with the institution until his death, — in all, from 1834 to 1892, a period of fifty-eight years, thus exceeding by three years the term of Tutor Flynt (1699-1754), hitherto regarded as the College Nestor.

It must have been a severe ordeal to a young man to succeed such a brilliant lecturer as Professor Farrar; but the event showed that, although a lecturer of a very different type, Professor Lovering's instruction was no less effective than that of his celebrated and popular predecessor. Professor Lovering delivered nine courses of twelve lectures each before the Lowell Institute, and the first four of these, given at the Odeon on Federal Street between 1840 and 1844, the writer attended, and remembers distinctly how instructive and popular they were. Professor Lovering had great clearness of thought and singular definiteness and felicity of expression. He was apt in illustration, and a quiet humor often enlivened what would have been otherwise a dry demonstration. He gave most careful attention to the mechanical preparation of his lectures, and his experiments rarely failed of success. Besides his regular college lectures, during term time always one and usually two a week for a long period of years, and the lectures at the Lowell Institute above referred to, Professor Lovering gave shorter courses at the Smithsonian Institution in Washington, the Peabody Institute of Baltimore, and the Charitable Mechanics'

Institution of Boston, and one or more lectures in many towns and cities of New England.

The wonderful clearness and elegance of exposition so conspicuous in Professor Lovering's lectures appeared also in his monographs and popular essays on scientific subjects. These are very numerous, and are models of scientific style. They are scattered through various serial publications, and are probably known to but few of the present generation; but they represent his very best work, and in justice to his memory they ought to be collected and reprinted. Besides their intrinsic value as the literary work of a very successful teacher, they are valuable material for the history of science. Professor Lovering's long career covers a period of wonderful development in all departments of physics, not simply in the discovery of new facts, but also in the change of aspect under which the old facts are regarded. Our late colleague was a broad scholar, not only familiar with the past history of every branch of his subject, but also accustomed to look at facts from all sides. If a student who had fallen into the rut of a system went to him with a difficulty, — perhaps insuperable on that theory, — he would surmount the difficulty by taking the man out of the rut, and thus enabling him to look at the facts from a different point of view. How different would be our judgment of the alternating phases in the past history of science, — of the labors of the alchemists, for example, — if we could only see the facts as our fathers necessarily regarded them; and the most striking feature of Professor Lovering's essays is the circumstance that the point of view from which he writes is made so clear. Moreover, a comparison of the earlier essays with the later shows how the point of view changed, and that the author, acute scholar as he was, had closely followed the change.

The following contemporary notices fully justify the writer's estimate of these occasional essays, which are enumerated in the catalogue of his publications at the end of this notice. A scholar of high scientific eminence has recently written of these essays, that they impressed him as few others had ever done. "It will surprise him to know it; yet it is true that the ideas then presented, and with an elegance worthy of their breadth and power, affected the whole tenor and tendency of my thoughts, and thus of my subsequent life." And he compares the style of parts of them with that of the most classic passages in Babbage's Ninth Bridgewater Treatise.

So also Mr. R. W. Emerson published the following notice in "The Dial": "We rejoice in the appearance of the first number of this quarterly journal edited by Professor Peirce. Into its mathematics we have not ventured; but the chapters on Astronomy and Physics we read with great advantage and refreshment. Especially we thank Professor Lovering for the beautiful essay on the 'Internal Equilibrium and Motion of Bodies,' which is the most agreeable contribution to scientific literature which has fallen under our eye since Sir Charles Bell's work on the hand, and brings to mind the clear, transparent writings of Davy and Playfair."

Professor Lovering was not a writer of books, but he was an editor of very large experience. He was co-editor with our late colleague, Professor Benjamin Peirce, of the "Cambridge Miscellany of Mathematics, Physics, and Astronomy," published at Cambridge in 1842 and 1843, and devoted to pure and applied mathematics. He edited fifteen volumes of the Proceedings of the American Association for the Advancement of Science, also six volumes of the Memoirs and three volumes of the Proceedings of this Academy, and earlier, in 1842, a new edition of Farrar's Electricity and Magnetism. In 1873 he was the President for the year of the American Association, and in his reception address at Portland he said: "Few of us can aspire to the honor of being discoverers of the laws of nature in the highest sense of that phrase. But no one, however humble his capacities, or however limited his opportunities, who labors for science, will fail to advance it." This well expresses the attitude of our colleague towards his profession. He was not a born investigator, but one whose path in life was determined by force of circumstances, rather than by natural predilections. He was primarily a scholar, and the great service which he rendered to science was that of a scholar and a teacher, and not that of an experimenter. At the present day, courses of research in all departments of study are the latest fad at many of our higher institutions of learning; but excepting always the few highly favored men of the race to whom an unusual scientific insight has been given, it may be a question whether the broad scholar does not exert a greater influence on the advancement of knowledge than the average specialist.

But although Professor Lovering seems to have had little inclination to undertake original experimental investigation in Physics, he did a very large amount of work in observing and correlating facts. He was associated with the late Professor William C. Bond in the management of the primitive astronomical observatory first located at Cambridge in the dwelling-house still remaining on the corner of Quincy and Harvard Streets, and there took part in that concerted onset on the problem of the earth's magnetism instituted by Humboldt and Gauss, and continued throughout the British Empire for several years under the direction of the Royal Society of London. An appeal was made to various academies and men of science in this country to co-operate in the work, and the appeal was responded to by the Magnetic Observatory at Philadelphia under the care of the late Professor Bache, and by the American Academy of Arts and Sciences in Boston, who supplied the Cambridge Observatory with the requisite instruments. The plan of the Royal Society involved, besides frequent regular daily observations, an almost continuous watch on the magnetic needle during one day of each month. On these days, called term days, observations were made every five minutes on three different instruments, day and night. The chief burden of all this work fell on Professor Lovering, although he was greatly assisted, not only in the observations themselves, but also in their reduction and in the mathematical discussion of the results, by Professors Bond and Peirce and a few competent undergraduates. Of these last, the late Thomas Hill, afterward President of Harvard College, and Benjamin A. Gould, the present distinguished astronomer, deserve special mention.

Professor Lovering's experience in this famous magnetic campaign must have familiarized him with the magnetic disturbances accompanying the auroral discharge, and thus led him to discuss the mooted question of the periodicity of the aurora. His study of this problem was the most considerable work of his life. It involved the collating and discussing of an immense number of more or less indefinite observations, and the mere presentation of the result of this long and laborious investigation occupies over 350 pages of the quarto Memoirs of this Academy, New Series, Vol. X. Part I. In this memoir, Professor Lovering clearly defined the secular periods of the aurora, and also showed that no apparent connection could be traced between the secular periodicity of the aurora and the secular changes of the earth's magnetism, the periods of sun-spots, fire-balls, or earthquakes, or any other secular changes with which the aurora had been associated by various physicists. As he writes in this memoir, "A lesson of caution against hasty conclusions on subjects of such complexity may be drawn from the fact, that whereas Boné favored the conclusion that the aurora goes hand in hand with the earthquake, and whereas

Wolf had decided, though from data afterwards acknowledged to be insufficient, that years rich in sun-spots corresponded to years rich in earthquakes, Kluge, from a more searching examination and the use of larger materials, finds a periodicity for earthquakes as long as that which governs the sun-spots and magnetic disturbances, but with maxima and minima reversed." We quote this as an indication of our colleague's judgment and caution in the discussion of observations, and although the investigation did not lead to the discovery of unsuspected relations, yet the negative results reached were of the greatest importance, and the memoir just quoted may be referred to in our transactions with pride, as an example of great thoroughness in the collection of materials, and of remarkable freedom from bias in the discussion of results.

Between 1867 and 1876 Professor Lovering was connected with the United States Coast Survey, and had charge of the computations for determining differences of longitude in the United States, and across the Atlantic Ocean, by means of the land and cable lines of telegraph. The most important and interesting portion of the work which he did in this connection is discussed in a paper "On the Determination of Transatlantic Longitudes by Means of the Telegraphic Cables communicated to the Academy, January 29th, 1873," by permission of the Superintendent of the Survey, and published in the Memoirs, New Series, Vol. IX. page 437.

As might be expected from the character and direction of his scientific work, Professor Lovering had marked executive ability, and in all such relations he was in the highest degree methodical, accurate, and just. During 1853–54 and from 1857 till 1870 he was Regent, then the second executive officer of Harvard College. During this period he kept with his own hands such full and accurate accounts of the merits and demerits of each undergraduate that the Faculty could make his reports the basis of action with entire confidence, while at the same time in dealing with the students he showed such just discrimination and kindly appreciation that he gained their universal confidence and esteem.

When the Jefferson Physical Laboratory was opened, in 1884, Professor Lovering was appointed its "Director," and during the four years of his administration made "Annual Reports" of its activities. To this laboratory he carried the very large and valuable collection of philosophical apparatus which he had gradually accumulated during his long period of service as Hollis Professor. Mr. Lovering took great pleasure and a just pride in this collection. When he entered upon his office, there was already in the possession of his department a no inconsiderable number of philosophical instruments, some of which had a real historical interest, but they did not meet the requirements of a more modern science. Only a small annual appropriation could be obtained for the expenses of his lectures; but by carefully husbanding the resources, and doing all the mechanical work with his own hands, he was able from time to time not only to purchase the indispensable articles, but also to procure all the novelties as they appeared. He judiciously used his large knowledge and judgment in the original selection, and by constant watchfulness prevented the apparatus from deteriorating, and thus during his long term of service he brought together one of the most complete cabinets of physical apparatus in this country. Nothing delighted him more than some new mode of illustrating a recondite principle in a striking way, and every year, at the meeting of the old Scientific Club of Cambridge he would delight his associates also by bringing forward and explaining some such piece of apparatus, and he rose to the highest point of enthusiasm when he made it to appear that the paradoxes of science were no paradoxes at all, but the necessary unfoldings of fundamental laws.

Besides his uninterrupted work for the College, Professor Lovering discharged other executive duties in which he exhibited his usual faithfulness and good judgment. From 1854 to 1873 he was the Permanent Secretary of the American Association for the Advancement of Science, — an office which requires an unusual amount of executive skill, besides tact and affability. On the Permanent Secretary devolve the arrangements for the annual meeting, the collection and disbursement of the funds, and the publication of the yearly volume of Proceedings. It is all important that he should commend the Association to the successive communities where it meets, and commend himself to the local committees. All this service Professor Lovering rendered with great success, and carried the society through the disintegrating period of the Civil War, when its continued life seemed impossible, and so skilfully managed its finances as not only to print a volume of Proceedings every year, but also to leave in the treasury at the end of his term of office a valuable stock of publications and a goodly cash balance. On resigning this office, Mr. Lovering was elected President of the Association, and served as such at the Portland meeting of 1873. Both his reception and his retiring addresses were admirable in thought as well as in spirit, and are excellent examples of the best use of idealism in science.

In the first of these he said: "It is impossible for the man of science to serve two masters, the Kingdom of Nature and Mammon. It is a dangerous thing for him to be thinking of the utility of his discoveries, or of the pecuniary profit which may be made out of them." And in the second he adds: "Science is not destructive, but progressive; while its theories change, the facts remain. Its generalizations are widening and deepening from age to age. We may extend to all the theories of physical science the remark of Grote which Challis quotes in favor of his own: 'Its fruitfulness is its correctibility.' Instead of being disheartened by difficulties, the true man of science will congratulate himself, in the words of Vauvenargues, that he lives in a world fertile in obstacles. Immortality would be no boon if there were not something left to discover, as well as to love."

Professor Lovering was also for some years one of the trustees of the Tyndall Fund for the endowment of research in physics, and during the last few years of his life he was one of the Trustees of the Peabody Museum of American Archæology and Ethnology.

Professor Lovering was long and intimately associated with our Academy. He was elected Fellow on January 30, 1839, and the only surviving member on our list whose election antedates his is our honored colleague, Dr. O. W. Holmes. From 1851 to 1872 he was a member of the Committee of Publication. From 1847 to 1868, and again from 1878 to his death, he was a member of the Rumford Committee, and during the greater portions of these periods its chairman, directing its deliberations and inspiring a proper caution in the expenditure of the funds as well as in the bestowal of the medals under its charge. From 1852 to 1863, and again from 1865 to 1868, he held a place on the Council of the Academy by annual election, and during the rest of his life *ex officio*. From 1869 to 1873 he was Corresponding Secretary. From 1873 to 1880 he was Vice-President, and from 1880 to his death President. Thus our late colleague's membership has covered fifty-three of the one hundred and twelve years which have passed since the Academy was incorporated, under the Presidency of Governor James Bowdoin, in 1780. During this long period, nearly one half of its whole history, Professor Lovering through his force of character and commanding knowledge exerted a controlling influence in its affairs. For many years he superintended its publication, and the prosperity of our society during the second half-century of its life was in no small measure due to his fostering care. Mr. Lovering was also a member of the National Academy of Sciences, of the American Philosophical Society of

Philadelphia, of the California Academy of Sciences and of the Buffalo Historical Society. In 1879 he received from his Alma Mater the degree of Doctor of Laws.

Professor Lovering was pre-eminently a social man, and any notice of him would be incomplete that did not allude to this genial phase of his character. He was one of the few men who could hold his opinions and maintain his position without personal animosity or unfriendly feeling, could favor without partisanship, could oppose without bitterness. He never would quarrel, and, as he once said to the writer, it takes two to make a quarrel and the other man only counts one. Besides a frank cordiality and kindliness of greeting which made him very accessible, he had a fund of dry humor, which not only enlivened intercourse, but often gave force to an argument. Not unfrequently in meetings of the College Faculty he would turn a stupid debate, and exhibit a question in its real absurdity, by a witty remark. There was also a straightforwardness, integrity, and truthfulness about his intercourse which inspired confidence and warmly attached him to his friends. He was perfectly just and singularly free from bias, and in any question involving rectitude or faithfulness you could always count on him. He was faithful to every duty, and conscientiously discharged every obligation. He rarely, if ever, missed an appointment, and whatever he undertook, however unimportant, he did with all his might.

Besides attending and keeping up the spirit of the Cambridge Scientific Club above referred to, of which he was one of the original members, he was uniformly present at the meetings of the Thursday Evening Club in Boston, and often contributed to its proceedings. He very greatly enjoyed those meetings, and his communications were always esteemed by the members. He had the happy faculty of popularizing a subject without degrading it. He could present a problem so that his audience could follow as far as he led, and understand why he did not attempt to lead them further. His discourse was always free from trivialities or redundances, and his hearers could appreciate the grandeur of the mountain all the better because they had not made a fruitless attempt to climb it.

It was a very fitting tribute to Professor Lovering's warm social nature, that at the close of his active duties, in 1888, a banquet should be held in honor of his fifty years' service. It was the spontaneous offering of classmates, associates, pupils, and friends, and it afforded him the highest satisfaction. Besides the social pleasures and warm eulogiums of the time, the occasion led to two enduring memorials; first, a silver teapot, (copied from one formerly used by Tutor Flynt, now in the possession of Dr. O. W. Holmes,) which will be handed down as an heirloom in his family; and, secondly, a portrait painted by Linden Smith, which will hold his likeness on the walls of Memorial Hall.

Professor Lovering was married in 1844 to Sarah Gray Hawes of Boston, and his wife, with two sons and two daughters, survive him. Since retiring from active work, he has passed four serene and happy years. He several times said to the writer, "You don't know what a pleasure it is to be relieved from stated duties, and to have full command of your time. I have plenty to do, and never have an idle moment." Through great prudence and thrift he had laid aside a sufficient competency to relieve him from all pecuniary anxieties and his friends had hoped that he might long pass the full term of fourscore years. His wonderful vitality and singular immunity from disease encouraged this hope. He said to his classmate, Dr. Morrill Wyman, who had been his family physician for half a century, and who was feeling his pulse during his last illness, "No one has felt my pulse before since I was a child." But it was not to be. A severe cold complicated by the prevailing epidemic attacked the heart, and the end came in the early morning of January 18, 1892. The change was peaceful, and without pain.

The following catalogue of Professor Lovering's publications is taken from the College Class-book entitled "Memorials of the Class of 1833 of Harvard College, prepared for the Fiftieth Anniversary of their Graduation by the Class Secretary, Waldo Higginson"; and preceding the catalogue the Secretary states that it was furnished by Professor Lovering. The present writer has only added a few items of papers which to his knowledge have appeared since.

1. An Account of the Magnetic Observations made at the Magnetic Observatory of Harvard College. In Two Parts. (Memoirs of the American Academy, vol. ii., 1846.)
2. On the Secular Periodicity of the Aurora Borealis. (Ibid., vol. ix.)
3. On the Determination of Transatlantic Longitudes by Means of the Telegraphic Cables. (Ibid., 1867.)
4. Catalogue of Auroras observed, mostly at Cambridge, after 1838. (Ibid., vol. x., 1868.)
5. On the Periodicity of the Aurora Borealis. In Two Parts. (Ibid., with plates, 1868.)

6. On the Causes of the Difference in the Strength of Ordinary Magnets and Electro-magnets, of the same Size and Shape. (Proceedings of the American Academy, vol. ii.)
7 On the Law of Continuity. (Ibid.)
8. On the Aneroid Barometer. (Ibid.)
9. Electrical Experiment. (Ibid., vol. iv.)
10. On the Connection of Electricity with Tornadoes. (Ibid., vol. ii.)
11. On Coronæ and Halos. (Ibid.)
12. On the Spectroscope. (Ibid., vol. iii.)
13 On the Bioscope. (Ibid.)
14. Apparatus for Rapid Rotations. (Ibid.)
15 Shape of Luminous Spots in Solar Eclipses. (Ibid.)
16. Notice of the Death of John Farrar. (Ibid.)
17 Notice of the Death of Melloni. (Ibid.)
18. New Apparatus and Experiments in Optics and Acoustics. (Ibid.)
19. Arago's Opinion of Table-Moving. (Ibid.)
20. On Fessel's Gyroscope. (Ibid.)
21. Apparatus to regulate the Electric Light. (Ibid.)
22. Does the Mississippi River flow Up-hill? (Ibid.)
23. Report on Hedgcock's Quadrant. (Ibid.)
24. On the Boomerang. (Ibid., vol. iv.)
25. Report on Meteorological Observations. (Ibid.)
26. On the Ocean Cable. (Ibid.)
27. On the Polarization of the Light of Comets. (Ibid.)
28. Report on the Polar Expedition of Dr. I. I. Hayes. (Ibid.)
29. On Records of the Aurora Borealis. (Ibid.)
30. First Observations on the Aurora in New England. (Ibid.)
31. Notice of the Death of Biot. (Ibid., vol. ii.)
32. On the Velocity of Light and the Sun's Distance. (Ibid.)
33. Notice of the Death of O. M. Mitchell. (Ibid.)
34. On the Optical Method of studying Sound. (Ibid., vol. vii.)
35. On the Periodicity of the Aurora Borealis. (Ibid., vol. viii, 1873.)
36. On the French Republican Calendar. (Ibid.)
37. Application of Electricity to the Motion of Tuning-Forks. (Ibid.)
38 On Optical Meteorology. (Ibid.)
39. On Transatlantic Longitudes. (Ibid.)
40. Notice of the Death of William Mitchell. (Ibid.)
41. Notice of the Death of Faraday. (Ibid.)
42. Notice of the Death of David Brewster. (Ibid.)
43. Notice of the Death of J. W. F. Herschel. (Ibid.)
44. Notice of the Death of Christopher Hansteen. (Ibid., vol. ix.)
45. Notice of the Death of Auguste A. de la Rive. (Ibid.)
46. Notice of the Death of James Walker. (Ibid., vol. x.)
47 Notice of the Death of Joseph Winlock. (Ibid., vol. xi.)
48. Notice of the Death of Alexis Caswell. (Ibid., vol. xii.)

49. Notice of the Death of John H Temple. (Ibid., vol. xiii.)
50. Notice of the Death of Joseph Henry. (Ibid., vol. xiv.)
51. Notice of the Death of H. W. Dove. (Ibid., vol. xv.)
52. Address as President on presenting the Rumford Medal to J. Willard Gibbs. (Ibid., vol. xvi.)
53. Anticipations of the Lissajous Curves. (Ibid.)
54. Notices of the Deaths of Richard H. Dana, of Edward Desor, and of John W. Draper. (Ibid., vol. xvii.)
55. Notice of the Death of Sir Edward Sabine. (Ibid., vol. xix.)
56. Address of the President on presenting the Rumford Medal to H. A. Rowland. (Ibid.)
57. Address as President on presenting the Rumford Medal to S. P. Langley. (Ibid., vol. xxii.)
58ª. Notice of the Death of Gustav Robert Kirchhoff. (Ibid., vol. xxiii.)
58ᵇ. Address as President on presenting the Rumford Medal to A. A. Michelson. (Ibid., vol. xxiv.)
58ᶜ. The "Mécanique Céleste" of Laplace, and its Translation by Bowditch. (Ibid., vol. xxiv.)
59. On the Electro-dynamic Forces. (Proceedings of the American Association for the Advancement of Science, vol. ii.)
60. On a Curious Phenomenon relating to Vision. (Ibid.)
61. On a Singular Case of Interference in the Eye itself. (Ibid., vol. vii.)
62. On a Modification of Soleil's Polarizing Apparatus. (Ibid.)
63. On the Australian Weapon called the Boomerang. (Ibid., vol. xii.)
64. On the Optical Method of studying Sound. (Ibid., vol. xvi., 1868.)
65. On the Periodicity of the Aurora Borealis. (Ibid.)
66. Sympathetic Vibrations between Tuning-Forks and Stretched Cords. (Ibid.)
67. On Methods of illustrating Optical Meteorology. (Ibid., vol. xix., 1871.)
68. On Sympathetic Vibrations. (Ibid., vol. xxi., and Journal of the Franklin Institute, May, 1873.)
69. Addresses as President at the Portland Meeting of the American Association for the Advancement of Science. (Proceedings of the A. A. A. S., vol. xxiii.)
70. On a New Way of illustrating the Vibrations of Air in Organ-Pipes. (Ibid.)
71. Address as Retiring President. (Ibid.; republished in the Popular Science Monthly, American Journal of Science, and the London Philosophical Magazine.)
72. On a New Method of measuring the Velocity of Electricity. (Proceedings of the American Association for the Advancement of Science, vol. xxiv.; also Journal de Physique, tome vi.)
73. Shooting Stars (American Journal of Science, vol. xxxv.)
74. The American Prime Meridian. (Ibid., N. S., vol. ix., 1850.)

75. The Aneroid Barometer. (Ibid.)
76. On the Velocity of Light and the Sun's Distance. (Ibid., N. S., vol. xxxvi.)
77. Melloni's Researches on Radiant Heat. (American Almanac, 1850.)
78. Animal Electricity. (Ibid., 1851.)
79. Recent Discoveries in Astronomy. (Ibid., 1852.)
80. Comets. (Ibid., 1853.)
81. Atmospherical Electricity. (Ibid., 1854 and 1855.)
82. Lightning and Lightning-Rods. (Ibid., 1856.)
83. Terrestrial Magnetism. (Ibid., 1857.)
84. Theories of Terrestrial Magnetism. (Ibid., 1859.)
85. On the Boomerang. (Ibid., 1859.)
86. On the Aurora Borealis and Australis. (Ibid., 1860.)
87. On Meteorology. (Ibid., 1861.)
88. On the Pressure of the Atmosphere and the Barometer. (Ibid., 1862.)

REVIEWS, ETC.

89. Guyot's Physical Geography. (Christian Examiner, vol. xlvii.)
90. Humboldt's Cosmos. (Ibid., vol. xlviii.)
91. Scepticism in Science. (Ibid., vol. li.)
92. Spiritual Mechanics. (Ibid., vol. lv.)
93. Thompson and Kaemtz on Meteorology. (North American Review, vol. lxxi.)
94. Elementary Works on Physical Science. (Ibid., vol. lxxii.)
95. Michael Faraday. (Old and New, vol. i.)
96. Reports on Lighthouses. By Benjamin Peirce and Joseph Lovering. (Journal of the Franklin Institute, vol. xviii.)
97. On the Internal Equilibrium and Motion of Bodies. (Cambridge Mathematical Miscellany, vol. i.)
98. On the Application of Mathematical Analysis to Researches in the Physical Sciences. (Ibid.)
99. Encke's Comet. (Ibid.)
100. The Divisibility of Matter. (Ibid.)
101. Boston and Science. (Memorial History of Boston, vol. iv.)
102. Article on the Telegraph. (American Cyclopædia, last edition.)
103. Address at the Dedication of the Mural Monument to the Memory of Dr. James Walker, in the Harvard Church, Charlestown.
104. Notice of the Death of F. A. P. Barnard. (Proceedings of the American Academy, vol. xxiv.)

SUBJECTS OF LECTURES AT THE LOWELL INSTITUTE.

1840–41. Electricity and Magnetism.
1841–42. Mechanics.
1842–43. Astronomy.

1843–44. Optics.
1845–46. Astronomy.
1853–54. Electricity and Magnetism.
1859–60. Astronomy.
1865–66. Light and Sound.
1879–80. Connection of the Physical Sciences.

GEORGE HINCKLEY LYMAN.

Dr. George Hinckley Lyman, Resident Fellow of the Academy, was born in Northampton, Mass., July 17, 1819, the son of Jonathan Huntington and Sophia (Hinckley) Lyman. He was educated at the famous Round Hill School in Northampton; but on account of ill health he was obliged to pass several years in Ohio and other Western States before beginning his professional studies in the University of Pennsylvania, at Philadelphia, where he took his degree of M. D. in 1843. Wishing to qualify himself thoroughly for the practice of his profession, he devoted more than the usual time to advanced study and clinical observation in the great hospitals of Europe, before returning to establish himself in Boston. Here he at once attracted attention through the publication of two Essays, — on "Non-Malignant Diseases of the Uterus," and on the "History and Statistics of Ovariotomy," — which had gained prizes offered by Medical Societies as being valuable contributions to the knowledge of the profession, and marked by the wise discrimination and candor shown in the discussion of their subjects, to which was added the charm of clearness and elegance of style.

The early promise thus given of Dr. Lyman's career was amply fulfilled. His thorough training, quickness of observation, and good judgment, with his faithful ministrations and ready sympathy, invited and retained the confidence of his patients of high or low degree.

But his success as a physician did not make him heedless of the claims of his country. At the outbreak of the Civil War, in 1861, he volunteered his services to Governor Andrew of Massachusetts, and, in co-operation with Surgeon General Dale, become his efficient adviser in the organization of a suitable surgical and ambulance service for the departing troops. Nor did he linger in the rear. As these went to the front, he went to share their dangers and alleviate their sufferings.

Standing first on the list of candidates examined by the Medical Army Board of Washington, he outranked during the war all the appointees from civil life. He was soon assigned as Medical Director of the Division commanded by General Fitz John Porter, and afterward of the entire Fifth Corps, comprising twenty-six thousand men. Prostrated for a time by the severe fatigues and exposures ensuing after the exhausting marches and sanguinary battles at Gaines's Mill and elsewhere, Dr. Lyman was upon his recovery appointed one of six Medical Inspectors of the Army, with the rank of Lieutenant Colonel; and ordered to inspect the great hospitals at Baltimore, Washington, Philadelphia, and New York. Next he was given supervision of the Medical Department which included Kentucky, Tennessee, West Virginia, and Ohio, and as far southward as our army lines extended; finding in Nashville and some other large cities the churches, warehouses and many dwellings overflowing with the wounded. Afterwards he travelled more than three thousand miles by rail through the Department of the East, to investigate alleged hospital abuses; and was then transferred to the Department of the South, to inspect the hospitals, and to await the arrival of Sherman's army on its march to the sea, and report on its sanitary condition.

In the important positions he held on the Army surgical staff, Dr. Lyman worked *indefatigably to organize and to improve* the supply, ambulance, and hospital services.

At the close of the war, Dr. Lyman by no means reposed on his laurels, but returned with fresh zeal to his home life and professional work. In addition to his private practice, he filled until his decease the post of Visiting Physician to the Boston City Hospital, where his wide experience, his devotion to the patients under his charge, and his courteous relations with his colleagues of the staff, caused his loss to be deeply felt.

In 1875 Dr. Lyman delivered the Annual Oration before the Massachusetts Medical Society, on "The Interests of the Public and of the Medical Profession"; in 1870 he was its Anniversary Chairman; and in 1879–80 he received the highest honors in the gift of the profession, in his election for the two years as President of the Society, where his administrative talent, and his tact, dignity, and courtesy as a presiding officer did much to promote its interests.

Dr. Lyman was one of the founders and officers of the Massachusetts Medical Benevolent Society, instituted to aid such worthy members of the profession, or their families, as had through illness or misfortune fallen into distress. He was also one of the founders of the American Gynecological Society, and an active member of the Boston Obstetrical Society, of the Boston Society for Medical Improvement, of the Military Historical Society of Massachusetts, and of the Military Order of the Loyal Legion of the United States. He was an Honorary Member of the Harvard Medical School Association, and for many years was vestryman of St. Paul's Church.

In the various societies for medical improvement of which Dr. Lyman was an honored, an active, and an interested member, his qualities as an original thinker and accurate observer, and his large experience, to which was added much aptness and conciseness in debate, gave weight to every expression of his opinions.

In his visits abroad during nearly a half-century of professional life Dr. Lyman had made the acquaintance of many medical and scientific men of celebrity; and he delighted in extending to some of these, visiting this country, his graceful welcome and hospitalities, to which his own cultivated taste in matters of literature and art gave additional charm.

Dr. Lyman was in no respect a passive man. Of active temperament, quick and independent in thought and deed, earnest in convictions, unchanging in friendships, with a high sense of honor, he was always ready to promote a good work, but impatient of wilful negligence or imposture. His busy career compelled him to limit his attention to matters more or less germane to his profession, rather than to undertake elaborate and minute scientific researches; but he solaced the intervals of a laborious professional life with literary enjoyments and when at times he contributed something for publication it was notable for clearness and elegance of diction, and bore the stamp of trustworthiness.

Dr. Lyman married, first, October 14, 1846, Maria Cornelia Ritchie, daughter of James T. Austin; she died in 1864, leaving two sons and two daughters. He married, second, February 13, 1879, Henrietta, daughter of Samuel T. Dana, who survives him.

Having gone abroad in the spring of 1890, Dr. and Mrs. Lyman passed the ensuing winter in Italy, and the summer in Switzerland and Paris. On reaching London in August, Dr. Lyman had an attack of facial erysipelas, from which he had four times previously suffered, and which ten years previously had been complicated with a deep-seated orbital abscess causing loss of vision in one eye. The same conditions now recurred, and were combined with embolism of the femoral artery. He early became unconscious, and died on the 19th of August, 1891. His interment took place at Mount Auburn, on the 2d of September.

DAVID HUMPHREYS STORER.

DAVID HUMPHREYS STORER was born in Portland, Me., March 26, 1804, and died in Boston, September 10, 1891. His father was Chief Justice of the Court of Common Pleas at Portland, and an elder brother became Chief Justice of the Supreme Bench of Ohio. Through his father he was descended from Governor Langdon of New Hampshire, one of the signers of the Declaration of Independence, and through his mother from Governor Dudley of the Massachusetts Bay Colony. Dr. Storer graduated at Bowdoin College in 1822, studied medicine in Boston under Dr. John C. Warren, and took his degree at the Harvard Medical School in 1825. He at once entered upon the practice of his profession in Boston, and after the hard struggle to which even talent is exposed in a strange city he gained position as one of the leading practitioners of Boston. In 1837, with Dr. Jacob Bigelow and others, he established the Tremont Street Medical School, a private school "which, as the germ of the present curriculum of Harvard, has borne much valuable fruit," but afterwards, in 1854, took the Chair of Obstetrics and Medical Jurisprudence in the Harvard Medical School, where he became Dean, in which capacity he served for many years.

His great success in the medical field has been properly recorded by his colleagues, and need not be further noticed here, since it was for his work in another department that he was chosen to the Zoölogical Section of the Academy, November 8, 1837.

Like most naturalists who have distinguished themselves in later life, his interest in natural history began at an early period. Entering college when not yet fourteen years of age, he came under the influence of Prof. A. S. Packard, for whom he retained through life a warm affection and admiration. At first mineralogy particularly interested him, and he greatly enjoyed the field excursions to mineral localities made with Professor Packard; the collections then made were afterwards given to one of his sons, and put to good service in teaching the first classes in the Institute of Technology.

Yet his taste for natural history at that early period was by no means confined to minerals; entomology engaged much of his attention, and he gave popular lectures on insects in the days when lyceum lectures were first instituted; he was also devoted to ornithology, and made at one time a large collection of birds' eggs; indeed, it was through his example and interest that his brother in law, our late associate, Dr. T. M. Brewer, became a student in this field. His taste for collecting extended even to coins. At one time he was in league with all the toll gatherers on the Boston bridges, and they kept for him any odd pieces of money which fell into their hands. This passion for numismatics, it may be added, appears to have been handed down to his descendants, one son being still deeply interested in the subject, and a grandson the Curator of the Coins belonging to Harvard University. The coin-collecting mingled curiously with his Natural History interests, and we are told that he persuaded the keepers of several sailor's boarding-houses to secure for him any coins, shells, or fishes which their guests might have obtained in foreign parts.

It was natural that he should join the Boston Society of Natural History, which he did immediately after its foundation in 1830, so that he has always been enrolled as one of the "original members," though he was not strictly such; his activity is attested to by his being chosen a few months later Recording Secretary, a post he held for nearly six years. At this time he appears to have been giving special attention to Mollusca, and as a number of other gentlemen at the same period in our city were also forming collections, it was doubtless from the enthusiasm born of this common interest that he ventured to issue the prospectus of a contemplated translation of Kiener's "Iconographie," then in course of publication in Paris; but for lack of support only one part of the translation ever appeared, an octavo of about a hundred and fifty pages, issued in 1837. His own collection, kept until his death, has recently been given to Bowdoin College.

It is apparent, then, that in his early manhood he had made a somewhat thorough acquaintance with more than one department of natural history, and this makes it natural that his name was mentioned (and, if he had permitted, would have been urged) by his friends for the post of Naturalist to the government exploring expedition under Captain Wilkes. It explains, too, his success in a field he had then hardly cultivated; for the turning point in his career as a naturalist came when, in 1837, as the result of a memorial of the Natural History Society to the General Court, the legislature authorized a Natural History Survey of the Commonwealth, and the Governor appointed Dr. Storer one of the Commissioners to prosecute it. The several commissioners divided the work between them, and as Dr. A. A. Gould, an older and more experienced malacologist, was naturally assigned the Mollusca, Dr. Storer undertook the description of the fishes and reptiles of the State. He had previously paid some attention to one of these groups, the fishes, as is shown by the justly severe criticism of Smith's list of our species which he published the year before in the

"Boston Journal of Natural History"; but it is probable that his special acquaintance with this part of our fauna only began at about that time, when he was appointed one of the Curators of the Society's museum. Yet three years thereafter he published his report upon both the groups, an octavo volume of two hundred and fifty-three pages. Considering that these were just the years in which he was one of the chief supports of the infant Tremont Street Medical School, which gave systematic instruction throughout the year (the Harvard Medical School only for the four winter months), that he had the care and toil of an engrossing profession, and that scarcely the nucleus of a collection existed when he began his work, the result is certainly surprising. Through all the spring, summer, and autumn months, from five o'clock in the morning until the breakfast hour, he might be found engaged at the Society's museum over his specimens, snatching the early hours out of a busy day; every day, too, found him in the markets and by the wharves, interesting the fishermen in his eager search for strange forms of fish; this contagious enthusiasm was one of the chief sources of his success.

It was a token of his interest in and appreciation of this work that Agassiz, when he first landed on our shores, went directly to Dr. Storer from the house of Mr. Lowell, through whose invitation he had come to America. Dr. Storer's house was for years the daily resort of Agassiz and his Swiss associates, and with them his children grew up on the most familiar terms.

This work upon our Massachusetts fishes and reptiles was thoroughly done, equal to the best work of the time, and, like several other volumes of the remarkable series published under the auspices of the State, will ever remain a work of special value. That it was not complete no one knew better than the author, and this doubtless it was which led him to continue his investigations with the purpose of revising, enlarging, and perfecting it. To this he devoted all the forced leisure of more than twenty-five years, publishing the work by instalments in the Memoirs of the American Academy, with excellent illustrations, between 1855 and 1867; afterwards issuing it separately, under the title of "A History of the Fishes of Massachusetts," as a quarto volume of two hundred and eighty-seven pages and thirty-seven plates.

In this work he redescribed, and with greater fulness, all the species from our waters, and elucidated their natural history with the greatest care, paying particular attention also to the economic side. His style is lucid and simple, his descriptions perfectly clear and well ordered, the synonymy carefully worked out. There is as yet no complete work of the kind for any part of the United States which surpasses it, and it will ever remain a land-mark in the ichthyological literature of the country; for it is a storehouse of facts, and it was the successful collecting and simple presentation of facts which made the volumes of several of the earlier commissioners — Harris, Gould, Storer, and Emerson — models of what natural history work of permanent value should be.

Dr. Storer's other considerable publication, the "Synopsis of the Fishes of North America," a quarto volume of nearly three hundred pages, published in 1846, is of less value, because distinctly a work of compilation, and he was not so skilled in the niceties of classification as in the descriptions of the different specific forms and the study of their histories; but it was the first considerable attempt to collate existing material, and as such it had its importance and convenience.

A man full of enthusiasm, and sympathy, fearless, impulsive and generous, high-minded, high-spirited, and with a noble scorn of anything mean, deceitful, or unjust, Dr. Storer endeared himself alike to pupils and associates. No one who has known him will forget the open, brilliant expression of his mobile countenance, his piercing, friendly eye, the quick, impulsive speech, full of force and geniality; he was a friend worth making a sacrifice for, and not to be forgotten. In 1829, he married Abigail Jane Brewer, sister of the ornithologist, the late Dr. T. M. Brewer, by whom he had three sons and two daughters. His wife died in 1885. His children survive him; two of his sons have distinguished themselves in science, and have been elected to membership in this Academy. Dr. Storer was the recipient of many honors in his medical profession, a member of many learned societies, and received from his Alma Mater the degree of Doctor of Laws in 1876. At the time of his death he was the oldest physician in Boston.

CYRUS MOORS WARREN.

Cyrus Moors Warren was born at Fox Hill, West Dedham, Massachusetts, January 15, 1824. He died at Manchester, Vermont, August, 13, 1891. He was a remarkably well defined example of that particular type of the American character which has been admirably depicted by Mr. Henry James in one of his best known novels. Bold, ready, persistent, intelligent, with unusual aptitude for business and for the affairs of ordinary life, and possessing decided administrative ability, he was none the less attracted instinctively by things high and excellent, and he sought faithfully, according to his lights, for the best which the world has to give. In his early years he devoted himself with untiring energy to the accumulation of property; but in middle life he gave himself up to the service of science with the same zealous ardor and with distinguished success. It then appeared that he cared for money only as a means to worthy ends, for he was liberal almost to a fault, and it was especially noticeable that he never shrank from expense when it appeared that by freely employing money some obscure point in science might be made clear. To his friends he was a constant reminder of the truth of the Old World dictum, "L'Américain ne se redoute à rien," and his work may well be regarded as a symbol of great things which will come to be when Americans such as he was shall more commonly than now happens give themselves up as he did to scientific pursuits.

This type is distinctively a product of our Western States. Many people at the East have no just conception of it. It was said indeed by a Boston lady who had been accustomed all her life to the society and the admiration of men wealthy, artistic, literary, and scientific, that she had never met or seen in her experience any such person as Mr. James's hero. But it was an easy matter to prove that she had not looked in the right place, even as Thoreau made answer to the seeker of arrow-heads by stooping to pick one up from the road on which they were walking.

Cyrus was the fifth son and the eighth child in the family of eleven children of Jesse and Betsey (Jackson) Warren, who came of old Massachusetts stock, of English origin, related in fact to the Warrens and Jacksons whose names have so constantly been conspicuous in the history of this State. Both of them belonged to well defined branches of the original stocks. Jesse Warren, the father, a man of decided ingenuity, was a blacksmith, who employed many men and carried on establishments which must have been large for those days. He became at length a manufacturer of ploughs also, which were esteemed in their time. He invented the so called swivel, or side-hill plough, and was, if not the first, among the first of New Englanders to make the working parts of ploughs of cast iron. Not having been pecuniarily very successful at Dedham, the elder Warren bought a farm at Peru, Bennington County, Vermont, in the very heart of the forests of the Green Mountains, and established also a foundry, plough-shop, and smithy there, in 1829, when the boy Cyrus was five years old. The wildness of the place may be conceived of from the facts that one night wolves killed a number of sheep in a field close to the house, and that the trunks of sweet-apple trees in the orchard were scratched by the claws of bears which came to gather the fruit. In doing so they left marks which made an abiding impression on the heart and the mind of the boy. It was in this region that the early childhood of our late associate was passed, and it was in such schools as the locality and the State could offer that his education was gained. When he was thirteen years old his father again moved, to Springfield, Vermont, and carried on an iron foundry there, which was totally destroyed by fire two years later, to the complete impoverishment of the family.

Cyrus, as he grew older, — together with his next elder brother, Samuel M. Warren, — became ambitious of obtaining a more liberal education, and both of them directed their energies earnestly to this purpose. For a number of years they supported themselves as best they could by any work they could find to do. They taught schools in the winters, and worked in hayfields during the summer vacations, pursuing their studies meanwhile at every opportunity, in the early morning and late at night, often under great difficulties, until the elder brother, in the hope of more speedily gaining the desired end, conceived an idea of improving the process of covering roofs with tarred sheathing, which was then struggling into existence. Samuel established works to this end at Cincinnati, Ohio, in 1846, and in the course of the next year asked his brother Cyrus to join him. A partnership was soon formed by the two brothers, with the understanding that, the moment the profits of the business should admit of it, the elder brother should be at liberty to study a profession, thus carrying out his fixed purpose from the beginning. The business succeeded so well that Samuel soon entered a lawyer's office at Cincinnati, and afterwards studied for a time at the Dane Law School in Cambridge. He graduated in due course from the Cincinnati Law School, and was admitted to the bar; but afterwards became a minister and preached at Brookline, Massachusetts, and for a number of years in London, England.

Cyrus remained meanwhile in Cincinnati, and he was married there in 1849 to Miss Lydia Ross. Other brothers had been called in to help carry on the roofing business, and in due course Cyrus, in his turn, found the purposed opportunity to devote himself wholly to study. He moved to Cambridge with his family in 1852, and entered the Lawrence Scientific School in the departments of Zoölogy and Chemistry. His first meeting with Agassiz at this time was an important event in his life. He never forgot the cordiality with which he was greeted, and he profited not a little from the advice which was then given him and from the encouragement he received. Agassiz quickly recognized the native force of the man, and sympathized with his thirst for knowledge. He was so well pleased with his efficiency that he urged him to devote his life to the study of natural history, and for a time Warren seriously thought of doing so; but chemistry proved to have a yet stronger claim upon him, and he thenceforth devoted himself to this branch of science. After working two years longer at Cambridge in the Chemical Laboratory, he took the degree of S. B., with high distinction, in 1855, having presented as a thesis the results of a study which he had made of the chemical composition of brain, with estimations of the amounts of sulphur, chlorine, and phosphorus therein contained. He commended himself to his teachers and examiners so heartily that immediately after graduation he was elected an honorary member of the Phi Beta Kappa, on nomination of Benjamin Peirce, seconded by Louis Agassiz, — being the first graduate of the Lawrence Scientific School to whom this honor was accorded.

Soon after graduating from the Scientific School, Warren took his family to Europe, and studied there during several years, first at Paris, then at Heidelberg under Bunsen, at Freiberg in Saxony, at Munich under Liebig, at Berlin under Heinrich Rose, and subsequently in London, — all this in a purely scientific spirit, and with thorough enjoyment of scientific research. It is noticeable that his work in Rose's laboratory on compounds of Zirconium and Titanium is far enough removed from any suggestion of utilitarianism. But though living in an atmosphere of pure science, and devoting himself earnestly to scientific study, he could not help noticing matters which might be of advantage to his brothers and himself in their business, and in this way he was led to the most important work of his life, — the separation and the study of volatile hydrocarbons.

The Brothers Warren had used originally for their roofing purposes the pitch of pine-tar; but the great business success of the firm seems to have depended largely upon their having turned their attention to the coal-tar of gas-works at a time when this material was absolutely without commercial value, and the makers of it were glad to give it away to any one who would remove it from their premises. They were the first in this country successfully to utilize on a large scale what had previously been regarded as a waste product. Thus it happened, long before any one had suspected that various substances obtainable from coal-tar would ultimately be put to highly important uses in the arts, that the Warrens got control of all the tar produced in New York City, and in several other of the larger cities of this country, and had made contracts for long terms of years with many of the largest gas-works, which gave them assured control of all the tar which might be produced. Hence, when the anilin dyes came into use, and a great demand arose for those portions of coal-tar naphtha from which these dyes were made, the Warrens were peculiarly favorably situated for producing the naphtha, and gained large profits by selling it.

Nothing could have been more natural than that the scientific member of the firm should turn his attention to the question how best to obtain these volatile products; and nothing marks the great inventive power of the man more clearly than the masterly way in which he solved this highly intricate problem. His process of "fractional condensation," as published in 1864 in the Memoirs of this Academy, is admirable alike as a means of scientific research and as a technological method. This memoir, with its explanatory diagrams, was widely copied in scientific journals, and an expert travelling in Europe in 1870 found the process in common use there in the distilleries of tar. In some instances the managers of these works knew that they were using Warren's invention, while others professed ignorance as to its origin, while freely admitting its excellence.

By means of this apparatus Warren dissected, so to say, in a most thorough and exhaustive manner the more volatile portions of the tars and oils which are obtained by the distillation of coal and of wood, as well as the naphthas of petroleum; and in so doing he solved wellnigh completely a chemical problem which had been regarded as one of the most intricate of the time. He claimed with justice for his apparatus that it enabled the chemist, occupied with the study of mixtures of volatile, non-decomposable liquids, to prove the negative as well as the positive, since by means of it it is easy to separate and obtain in a state of almost absolute purity the several components of the mixtures, and at the same time to prove that the mixtures contained no other substances than those actually isolated.

One important result of these researches was the wholly unlooked for discovery that the more volatile portions of Pennsylvanian petroleum contain two distinct series of homologous hydrocarbons (C_nH_{2n+2}), which run parallel one with the other. The boiling-points of the contiguous members of either series differ by 30° C. But while the several members of the first series boil at 0°, 30°, 60°, 90°, etc., the members of the other series boil at 8°, 38°, 68°, 98°, and so on. That is to say, the members of the two series boil at intermediate points, and the complete separation of them had been as good as impossible before the invention of Warren's method of fractioning. In point of fact, the existence of the double series had caused no little annoyance to chemists, in that they had been able to separate at one time some of the members of one series, and at other times members of the other series, with the result that much confusion prevailed. All uncertainty as to this matter was done away with at once by the publication of Warren's memoir. His discovery was seen to be true the moment attention was called to it. The causes of the previous confusion became manifest, and many of the earlier statements which had seemed to be conflicting were found to be fairly harmonious. He found furthermore that the less volatile portion of petroleum, instead of containing, as had been supposed, higher homologues of the bodies just now referred to, is composed of hydrocarbons of another class, C_nH_{n+2}; and of these olefines he separated three, boiling respectively at 175°, 196°, and 216° C. The difference between the boiling-points of contiguous members of this third series he found to be about 20°, and not 30°, as in the other series. Fortunately, an elaborate statement of these results will soon appear, for a completed memoir relating to them was found among Warren's papers after his death.

It is interesting to note the fact that the high degree of purity of the products obtained by Warren compelled him to take special pains to analyze them with particular accuracy. The ordinary methods of ultimate organic analysis had seemed sufficient for the comparatively impure substances studied by his predecessors, — perhaps because the errors due to the impurities known to be present were supposed to be larger than those inherent to the processes of analysis. But the inadequacy of the old methods was shown at once on attempting to study pure hydrocarbons by means of them, and Warren was forced to turn aside for a moment from his legitimate work in order to invent new methods of combustion in oxygen gas, and subsequently to devise a new method of determining the density of vapors.

The years devoted by Warren to the study of the hydrocarbons were the most fruitful of his scientific life. From 1863 to 1866, he had in Boston a thoroughly well equipped private laboratory, in which he gave himself up wholly to research. Eight papers were communicated by him to the Academy at that time, and were published in its Memoirs and Proceedings. Besides the discovery of new substances and the better definition of others which were already known, these papers describe novel and ingenious methods of his invention for the analysis of organic compounds, for the estimation of sulphur and of chlorine, and the determination of vapor densities. They contain among other things a critical discussion of the methods of determining boiling-points, and an exposition of the inaccurate methods and conclusions of some of his predecessors. One of his conclusions was, "that the boiling-point difference for the addition of $C H_2$ in homologous hydrocarbons is generally 30° C., — which is a much larger difference than had been commonly supposed."

Among the details of these researches will be found a statement relating to the separation of hydrocarbons from oil of cumin, which, though nothing more than an incident touched upon solely for the sake of elucidating the main line of the research, may well be cited as an example of neatness, completeness, and elegance in chemical work. Due account being taken of the very small amount of material at his disposition, this particular analysis well illustrates Warren's accuracy and his skill as a manipulator.

It is a matter for lasting regret that Warren was unable to carry out his plans for studying the large collection of pure volatile hydrocarbons which he accumulated during this period, and which for many years subsequently he kept in store. As an example of these things may be mentioned an extremely volatile, elusive, liquid sulphur compound from coal-tar, which he separated in a state of purity and had partially studied. Indeed, his process for determining sulphur in organic compounds was devised for the purpose of analyzing this substance. As it boiled freely at the temperature of melting ice, it had to be condensed by means of freezing mixtures. It was evidently a compound of considerable scientific interest. He called it provisionally "alliole." It is said that by taking pains to free benzol completely from this contamination, the commercial value of the benzol was increased. The purified benzol suited the anilin-makers better than the ordinary article.

From Boston, Warren moved to Brookline, and established another private laboratory there, which was for the time and for his purposes remarkably complete in its equipment. He fully intended to continue his scientific investigations, but so many adverse influences accumulated that he was unable to carry out his plan. For one thing, he was appointed to the Professorship of Organic Chemistry at the Massachusetts Institute of Technology, though he resigned the position after a year or two because it consumed too much of his time. He was continually appealed to also by his business associates, who besought him to help them in new enterprises, and to deliver them from difficulties, which he did frequently with signal success. His partners had missed him not a little during the term of his highest scientific activity; and afterwards, in a period of great commercial depression, they were only too anxious to be helped by "so good a man of business." It must be admitted that his associates had good cause to wish to have him always with them, for he was a conspicuously able and indomitable man, born to command success. To him the failure of an undertaking or loss of fortune meant little more than a new incentive to energy and to labor; and the customary and to-be-expected result of his activity was the recovery of all that had been lost, and more. Though ordinarily mild of manner and extremely good-natured, this determination of character was plainly written on his face; and it was remarked by an assistant in his Boston laboratory, in the winter of 1863, that Warren's mouth must have been copied for making up the photographs of General Grant, which were in that year beginning to be freely displayed.

As a matter of course, no man could long lead a life of such untiring activity. There was no apparent slackening of his mental powers even to the end, but his physical ability to labor sensibly diminished after the very severe strain and long-continued anxiety to which he was subjected during the period of commercial depression which succeeded the panic of 1873. As his physical powers diminished, he suffered frequently from severe nervous headaches, which were manifestly symptomatic of fatigue. But "it took much to discourage him," and to the last he kept himself accurately informed upon all matters of importance relating to a very large business, and did much of the thinking of the firm, and all of its most important correspondence. His partners and he himself knew well that he understood their affairs better than any one else, and could better than either of them attend to the business. The burden upon him was much increased in 1880 by the death of his brother, Herbert M. Warren, who was lost on the "Narragansett," in Long Island Sound. In 1888, when much enfeebled physically by overwork, he had a paralytic stroke, from which he never recovered. Two winters passed at Nassau, and a couple of summers spent in absolute rest in the Adirondacks and in Vermont, failed to restore him, and he died quietly in the summer of 1891.

It would be difficult to write in any way of Warren's scientific career, without making some mention of his business interests. For that matter, many of the results of his scientific labors are upon record, to be seen by every one; and it is instructive to consider in what respect this work was helped or hindered by the business relations. The fact that his firm so extensively controlled the coal-tar of the country forced them, as has been said, to prepare the naphthas therefrom when a demand for these substances arose, and afterwards, in like manner, they were called upon to produce large quantities of anthracene when this compound was required for making alizarin. At a much earlier period they had prepared naphthalin in a condition of almost absolute purity, with the ideas that this solid substance might be put to use by glass-blowers as a convenient fuel to throw into their "glory holes," instead of the "dead oil" used for producing a strong reducing flame, and that it could be moulded into candles, which might be burned out of doors in spring-candlesticks, — both of which plans were brought to naught by the speedy introduction of coal-oil and petroleum, and of paraffin obtained from these oils.

Another venture, which ended in failure, deserves mention as a matter of historical interest; namely, that the Warrens undertook to manufacture anilin colors in this country at a very early period (1862), when the price of these compounds was extremely high. To this end they built a factory at South Boston, and equipped it with costly and ingenious apparatus devised by C. M. Warren. This factory had actually been put into operation, and was producing nitrobenzol, when the price of the anilin dyes suddenly fell to a very low figure, from which point they have never risen again to anything like the former standard. The Warrens were thus compelled to relinquish their undertaking. The reduction in price had been brought about by certain English manufacturers who sought to crush a rival in that country.

From being engaged in all these enterprises Warren had constant opportunity to make note of points that specially needed elucidation in the behavior of the chemical substances operated upon, and he was doubtless able to gain time in many cases as regards his scientific investigations by making preliminary rough studies at the manufactory. Moreover, he could have at any time, for the asking, unlimited supplies of any materials he might wish to investigate, either in the crude or in the partially purified condition; and he could always be sure that his materials were precisely what they purported to be. It should be remembered always, when Warren's work on hydrocarbons is contrasted with that of his predecessors, that he had enormous advantages over most chemists both as to his methods and his materials. For example, it will be seen at a glance that it was easier for him than for most other investigators to make the discovery of his parallel series of hydrocarbons in the more volatile part of Pennsylvanian petroleum, because he had opportunity to operate upon materials which had never been subjected to any treatment with chemicals. His competitors, working upon commercial products which had been "purified" by agitation with oil of vitriol, were at a manifest disadvantage. There are published results of such investigations, which go to show that a large part of the members of one of the series had actually been removed in some way from the petroleum before it was subjected to scientific examination.

In the course of time, when their contracts for coal-tar had lapsed, and competition between the distillers of tar became sharp, the Warrens paid less attention than they had formerly done to this branch of their business, and turned their energies more particularly to the asphaltum of Trinidad, and to the rectification of this substance by a process which consists essentially in driving off some thirty per cent of water, which is entangled in the crude pitch as taken from the lake, and removing some other mechanical impurities by processes of settling or skimming. The product thus obtained, and known as refined asphalt, is used for electrical purposes, as well as for paving and for roofing. For some uses the purified asphalt is mixed with a certain proportion of petroleum residues that are left in the stills when crude petroleum is rectified.

In the carrying out of these changes Cyrus Warren took a lively interest and gave valuable aid. But it was characteristic of the man that during all the long period of business strain his mind was full of scientific interests and ideas. It is greatly to be regretted that the results of these cogitations and of the experiments made from time to time during this period have never been published. Warren himself felt that several of them should be made known to the world, and he fully intended in his last years to present to the Academy one or more papers relating to these matters. He never ceased to lament that the exigencies of business, in which he had become inextricably entangled, kept him from entire devotion to scientific pursuits. But perhaps the keenest of his regrets was felt when, after he was finally disabled, his physician forbade him to enter his laboratory to do a last work for science in gathering from his note-books and connecting the fragments of the more important labors which had been performed during the intervals of his business activity.

One of his ideas was to make a systematic scientific analysis of that portion of the heavier products of coal-tar which is known as anthracene oil. Anthracene itself is obtained from this grease by pressing the mass in a hydraulic press at a tolerably definite and constant temperature maintained by steam heat, by which means various crystalline substances other than anthracene are expelled; and Warren proposed to isolate each of these compounds by a process of fractional liquefaction or of methodized eliquation. He had gone so far as to have had constructed especially for this purpose, and at very considerable expense, a small compact hydraulic press which carried a copper jacket which was to be filled with water that could be kept at any desired temperature by means of gas lamps. The diameter of the jacket was enough larger than that of the plate of the press to admit of lamps being put under it to heat the water. In this way the mixture of crystals could be pressed again and again, at some one definite temperature, until the substance which remains solid at this temperature had become so pure that nothing more could be squeezed out from it; then the matters which had remained liquid at that temperature could be pressed at another temperature until another substance had been isolated, and so on as long as any of the material was left. This process seems to have reached an eminently hopeful stage of development, when work upon it was interrupted by increased business cares which followed the death of his brother, Mr. Herbert M. Warren. in 1880. It is evident that a manageable process of this kind would find ready applications in the study of waxes, fatty bodies, camphors, paraffins, and some resins, as well as in that of the heavy products of tar. Possibly even the very intricate problem as to the composition of the mixture of oxidized fatty acids, which are concerned in the technical process of currying leather, and in the old method of fixing the color known as Turkey-red upon cotton cloth, might be solved in this way.

This Academy was held by Cyrus Warren in profound respect. He was proud to be a member of it, and he appreciated very highly the scientific atmosphere which he found here. This remark is true also of our lamented associate Ferrel, whose early life had been akin to Warren's in many respects. It was a great pleasure to these men — independent and self-sustained though they both were — to be in touch with scientific associates. They knew that here at least their aspirations would be sympathized with and their efforts be justly appreciated; and it will be well for us all to remember how much such men may be encouraged by an organization of high tone and character competent to hold them steadily to their best ideals.

In Warren's last will and testament were found written the following words: —

"I give and bequeath to Harvard University fifty shares of the stock of the Warren-Scharf Asphalt Paving Company [now equal to $5,000 at the least], to be held by the said University, or to be sold and converted into money, and the proceeds thereof to be securely invested, and the income, dividends, interests, or profits of said stock, or of the proceeds of the same, to be devoted by the said University, in its discretion, to the promotion of chemical research, or the advancement of chemical science. . . .

"I give and bequeath to the American Academy of Arts and Sciences of Boston one hundred shares of the capital stock of the Warren-Scharf Asphalt Paving Company [equal to $10,000], the proceeds, dividends, and income thereof to be applied by the said Academy, its trustees or directors, in their discretion, for the encouragement and advancement of research in the science or field of chemistry. . . .

"I give and bequeath to said American Academy of Arts and Sciences fifty shares of the capital stock of the Warren-Scharf Asphalt Paving Company [equal to $5,000], the proceeds thereof to be applied to or towards a building fund for the purpose of erecting a building for the use of the library of said Academy, and for holding the meetings of said Academy; the same to be used in erecting such a structure when, in the opinion of the directors or trustees of said corporation, a sum sufficient shall be realized to justify such erection."

Papers by Cyrus Moors Warren.

1. Ueber einige Zirkonerde- und Titan-Säure-Verbindungen: —
   - A. Ein neues Schwefelsaures Zirkonerde-Salz, etwas Kali enthaltend.
   - B. Schwefelsaures Zirkonerde-Kali.
   - C. Schwefelsaures Titan-Säure-Kali. Poggendorff's Annalen, 1857, CII., p. 449.
2. On a Safety-lamp, for Laboratory Use. American Journal of Science, 1862, (2d series,) XXXIII. 275.
3. On a Process of Organic Elementary Analysis, by Combustion in a Stream of Oxygen Gas. Proc. Amer. Acad., VI. 251. (8 March, 1864.)
4. On a Process of Fractional Condensation; applicable to the separation of Bodies having small differences between their Boiling-points. Mem. Amer. Acad., IX. 121. (10 May, 1864.)
5. Researches on the Volatile Hydrocarbons: —
   - A. Hydrocarbons from Coal-tar Naphtha (p. 137).
   - B. Hydrocarbons from Oil of Cumin and Cuminic Acid (p. 149).
   - C. On the Influence of C_2H_2 upon the Boiling-points in Homologous Series of Hydrocarbons, and in some Series of their Derivatives; with Critical Observations on Methods of

taking Boiling-points (p. 156). Mem. Amer. Acad., IX. 135. (11 Oct., 1864.)

6. On a New Process for the Determination of Sulphur in Organic Compounds, by Combustion with Oxygen Gas and Peroxide of Lead. Proc. Amer. Acad., VI. 472. (14 March, 1865.)
7. On a New Process of Organic Elementary Analysis for Substances containing Chlorine. Proc. Amer. Acad., VII. 84. (31 Jan., 1866.)
8. Note on an Improved Apparatus for the Determination of Vapor Densities by Gay-Lussac's Method; being a Modification of Bunsen's Apparatus for measuring Aqueous Vapor. Proc. Amer. Acad., VII. 99. (10 April, 1866.)
9. Hydrocarbons of Pennsylvania Petroleum. American Journal of Science, 1868, (2d series,) XLV. 262.
10. (Posthumous.) On the Volatile Hydrocarbons in Pennsylvania Petroleum. Proc. Amer. Acad., XXVII. 56.
11. (Posthumous.) Note on a Criticism of the Author's Apparatus for Fractional Condensation. Proc. Amer. Acad., XXVII. 89.
12. (With F. H. Storer.) Examination of a Hydrocarbon Naphtha, obtained from the Products of the Destructive Distillation of Lime-soap. Mem. Amer. Acad., IX. 177. (9 Aug., 1865.)
13. (With F. H. Storer.) Examination of Naphtha obtained from Rangoon Petroleum. Mem. Amer. Acad., IX. 208. (9 Aug., 1865.)

SERENO WATSON.

Sereno Watson, a Fellow of this Academy, died at his home in Cambridge on March 9, 1892.

To most of his associates here he was known only as a regular attendant at our meetings, and an occasional contributor to our Proceedings, presenting his communications, which were of a technical character, by title.

His co-laborers in Natural History recognized him as a critical student in the department of Descriptive Phænogamic Botany, who enriched our volumes by the results of work of a high order.

Those who were engaged in neighboring fields of botanical investigation knew him as a faithful friend of few words. He was observed by them to carry on his researches in silence, seldom alluding to any special task in hand until it drew near completion, and even then only briefly. He was always ready to interrupt his studies to assist others in theirs; he would enter with unconcealed pleasure into the plans of others, but without ever speaking of his own.

Hence it happens that his intimate friends, when called upon to speak in his memory, think first of the reserve and silence in which he walked. The question arises in their minds at the outset, how far is one justified in breaking through a reserve which was unbroken by him, and revealing to others the features of his blameless and useful life. This question is answered in part by a few letters written by our friend to relatives, who were sometimes naturally importunate for details of his movements; some of these memoranda have been placed at my disposal for the execution of the present task. Beyond the limits of these letters, and of others sent me by his relatives and nearest friends, the present sketch will not venture to pass, until it reaches that period of his life which becomes a part of the history of American Botany.

Sereno Watson was born at East Windsor Hill, Connecticut, on December 1, 1826. His father, who had been a merchant in New York City, passed the last years of his life on a farm which he had inherited. On this farm Sereno's boyhood was passed, and here he developed a vigorous physique. Until his very last year, he was capable of sustained effort with little fatigue, from which it came to pass that he was wont to tax his strength to its utmost limit, often imprudently or with only slight regard to consequences.

The class in which he graduated at Yale, in 1847, was one of the largest and strongest at that period. In the words of one of his classmates, he "was always highly spoken of by those who knew him, but, as in later years, was so reticent as to his personal history that probably no one knew much about him." He was considered a good scholar. He distinguished himself especially in classics, taking prizes for Latin composition and translation.

In 1851 Watson wrote thus to a relative: "Three years and a half ago I graduated, and I doubt if there was ever a mortal cursed with more diffidence, less energy, or a head fuller of strange notions, and who, to make the matter worse, was so fully conscious of it all. The most that I have done since then has been partially to overcome these drawbacks to all success. On leaving college I knew not what to do. I had no predilection for any of the professions. The only course left open to me for getting a living was teaching school." To this work he went at once, and entered on a very varied experience. He taught common or district schools in Connecticut, Long Island, and Rhode Island, and in the Academies at Allentown, Penn., and Tarrytown, N. Y.

While teaching in Tarrytown, he wrote to a relative as follows: "My experience has taught me many a lesson which I probably would not soon have learned otherwise, and school teaching is not the least improving of schoolmasters. It is true I have lost time in gaining a profession, and shall lose more, but I scarcely regret it."

In the same letter he says: "I might say more of myself, my plans and my opinions. Many an episode, pleasing, displeasing, and ridiculous, might be inserted in the brief history upon the last two pages, but I dislike to speak so much of myself. It is perhaps a fault in my character, but I am rarely frank enough to confide to any one what only relates to myself alone."

Very early in his career as a teacher, he began the study of medicine, and, after the fashion of that time, with a practitioner as a preceptor, — at first with Dr. Watson of Scantic, and afterwards with Dr. Sill of Windsor. Of the next year he writes: "I lived through the winter of 1849–50 in New York," attending medical lectures at New York University, "and left with a much diminished respect for medical practitioners and professors in general, apart from medicine itself, which is a noble profession."

In 1851 he taught in Tarrytown; in 1852 he was at home, farming and studying.

Of the next few years, his brother Louis, a physician, gives the following account: "I wrote to him to come to Quincy, Illinois, where I was established, to study with me, see practice, and practise for himself, on cases that I could give him, and such as were likely to apply to him. He accepted, and was preparing to leave East Windsor, when his uncle, Rev. Dr. Julius A. Reed, of Davenport, Iowa, one of the founders of Iowa College, and one of the Trustees, induced him to go there instead, act as Tutor in the College, and teach in the Preparatory School. He reached there in September, and remained as Tutor till July, 1854. He then came to Quincy, studied in my office under my direction, and attended urgent calls in my absence. I was city physician at that time, and turned over to him most of that business, and gave him a small salary. He got some business in respectable families of his church, and more among the poor, from whom he collected but little. A physician of about seventy years fell and broke his femur. Sereno attended him throughout with good success, without once consulting me, and I think I knew nothing of it at the time. I remember only two cases of disease which he asked me to see with him, — both serious and complicated, and one of which proved fatal. His practice of medicine there was entirely satisfactory to his patients as far as I know. He was not legally qualified to practise, of course, but he was better informed than some who were. My brother Henry, late of Northampton, then in Greensboro, Alabama, president of an insurance and banking company, offered him a position as clerk or cashier, and he left Quincy in 1856, which was the end of his doctoring."

His brother Louis answers also a question which may be noted at this point: "As to his botanical studies I know but little. I suppose they were taken up among his studies for the medical profession. When he was at Quincy I occasionally picked up plants in the Mississippi bottoms, taking them to my office for examination. If I could not readily determine them by the only Botany I then had (Beck's), I referred them to him. He had more patience than I had, and determined them. When in the United States service in the Civil War, in the Southern Mississippi, Tennessee, and Missouri, I picked up plants unknown to me, and, having no books, I sent them to him to learn what they were, and received replies naming them."

He remained in the South engaged in insurance and banking until the breaking out of the Civil War. During this time he must have devoted a good share of his leisure to the examination of the plants around him, for he later manifested a great degree of interest in any rarities coming from that region.

Dr. Henry Barnard, then editor of the "Journal of Education," gave him on his arrival at the North, in 1861, some work connected with the Journal, all of which was satisfactorily done. Of this stage in Watson's life, the venerable Dr. Barnard speaks most affectionately. He recalls with vividness Watson's interest in plants, and his eager desire to aid beginners in their work of determining species. But he did not think of him at all as a botanist at this time; he seemed just as likely to turn his hand to one pursuit as to another.

In 1866, Watson entered the Sheffield Scientific School of Yale, at the age of forty, as a student, but not to pursue botanical investigations. He went there to carry on studies in chemistry and mineralogy. He impressed his teachers in these departments as being capable and diligent. The possible, or rather probable design for which these special studies were undertaken must have been to fit him for a residence in California, which he had now in mind. The studies had a practical turn. His nephew remembers distinctly that during this time they made a journey together to Loudville, Conn., to examine an abandoned lead and silver mine, and still another visit to an abandoned iron mine.

These facts are here mentioned not so much to indicate the range of his studies as to point out the thoroughness with which he endeavored to prepare himself for the next work in view. But he was now on the eve of a total and unforeseen change of plan, by which he soon entered on a sphere of activity in which all his previous training was utilized. This change of base and plan are best described in his own words. The account is thoroughly characteristic. It is dated San Francisco, April 28, 1867.

"The request in your last letter that I should 'open' would have received prompter attention had there been anything to say for myself beyond conjecture. There is at least this much certain at present, that I have left New England again and am safely landed in this capital city of the Land of Gold. I have been ready to start on short notice for several months, but one thing after another turned up which involved the possibility of my not coming at all, so that I was kept in a state of uncertainty, and not able to say definitely whether I was coming here or not. One proposition was made to me to take ten thousand dollars and go into the drug business at Selma, but this fell through. Another was to buy a saw-mill and go into the lumber business with Mr. Wemyss at Mobile. A week's delay of the mails flanked that movement. Mr. Barnard offered me a clerkship in the new Educational Department at Washington, of which he is appointed Commissioner, and this I declined. One Friday I found myself clear of all questions of the kind, and, to give no time for any more to come, I determined to take the next steamer, which sailed on Monday. To pack up, close up, say good by, and get to New York by Saturday evening, left of course very little spare time. I wrote no letters, and did not stop to see friends in East Windsor or Hartford, but made my escape by the flank, and am consequently now here. . . .

"I am not yet settled, and do not know where it will be nor at what business. I started with a dozen strings to my bow, some of which snapped at the first trial. I am confident that some of the rest will do better. I have no idea of going to the mines."

It appears that at first Watson thought of farming in California. Even in the early years after graduation from college he had contemplated taking a farm in Connecticut with his brother, and this occupation always had great attractions for him. But suddenly he gave up the idea of purchasing a farm in California, and started from Woodland across the Sierra Nevada to join the Geological Survey of the Fortieth Parallel. Doubtless he had heard something of the proposed survey from the leader of the expedition, Clarence King, who passed a part of the previous winter in New Haven.

He reached the camp on the Truckee River on a July night, coming in covered with dust, foot-sore, with his boots and pack slung over his shoulder, and presenting the appearance of one unused to rough mountaineering. But he would not rest, eat, nor wash until he had arranged with the chief of the party for some sort of work to do. He was at first put to plant collecting in connection with miscellaneous topographical work. The botanist of the expedition, Mr. Bailey, now Professor of Botany at Brown University, had been too ill to botanize in the desert, and this work fell naturally into the hands of Watson. Under date of August 18 he writes: "I am informed to-night of a change in my position. I have worked thus far without any pay beyond my expenses, and giving my special attention to botany, but I am now assured of a salary, small as yet, but better than nothing, and am detailed to the topographical department."

One of the members of the party writes: "Watson was an exceedingly hard worker, — on the tops of the mountains, out in the broad sage-brush flats, down in the cañons, and tramping amongst the hot springs and alkali soils for plants. What impressed me the first year was not only his energy, but the systematic way in which he searched all kinds of soils and exposures for variations in plant life."

Of him the leader of the expedition says: "He impressed me as a man of work, grimly and conscientiously in earnest. . . . He smiled only as a forced concession to humor. Everything pertaining to his duty was sacred. . . . He soon learned to ride, and after the first anxieties regarding his duties had worn off he began to enjoy the campaign life and the weird scenery with the greatest enthusiasm. Bailey grew more and more subject to the camp illness, and at last gave up and went home to the East. . . . I then installed Watson in charge of the Botany. He was then as nearly perfectly happy as I have ever seen a human being. There were periods of at least five minutes at a time when the hereditary New England grimness vanished from his face, and he wore a free, careless air, as if his grandfather might have come from at least as far south as Virginia. If these excessive moments were rare, the general tone had grown calmly happy, and so I believe he remained till his connection with the Fortieth Parallel ceased."

Another expression by his chief, states what was equally true of his herbarium investigations: "He worked without the least nervous excitement or hurry, but continuously, and for a calm man rather rapidly."

The report on the botanical studies, and the description of the collections made at this time, were prepared in the herbarium of Professor Eaton, at New Haven and at Cambridge. But one can see that the notes were made on the spot where the plants were found, and nothing was left for the memory to lose. Watson wrote thus in a letter concerning the scope of the collection: "My work is at Professor Eaton's house, where all my plants are. I spend from two to twelve hours a day upon them, and it is going to be an everlasting job to work them up. It is the best and largest collection that has ever been brought in by any government party, and promises to yield a fair proportion of new species."

The Report was published in 1871, and confirms fully the statement made in the note which I have read. Not only were the collections the largest, but the notes respecting the surroundings of the plants were more detailed than any that had ever been returned from our Western plains. The notes constitute a fund of information for those who would know the habits of our desert plants.

The last portion of the Report was prepared at Cambridge, in the Gray Herbarium that was his home from 1870. Here he attacked and solved some of the most puzzling questions regarding North American plants, and the results of these researches are given for the most part in the volumes of our Proceedings. His other investigations and his separate works are noticed in the bibliography which is appended to this sketch.

At the time he was taken ill, he was engaged in the attempt to complete the Synoptical Flora of North America, left unfinished by Dr. Asa Gray. For this work his extensive acquaintance with our Western Flora and his conservative views regarding nomenclature specially fitted him. For the most part his botanical practice and principles were in perfect accord with those of his predecessor. His maturity of thought, his wide training in many and diverse fields, and his independence in deciding questions seemed to render his service in the completion of the Synoptical Flora on the lines laid down by its designers absolutely indispensable. At present, the Flora stands as a broken column, twice interrupted in construction.

No sketch of Watson's life, however brief, would be complete without some mention of three journeys other than those of the Survey already described.

One of these was in behalf of the Forestry division of the Tenth Census. For a few friends he prepared a charming sketch detailing his adventures. The sketch gives a glimpse of the keen pleasure which he took in wandering, and his untiring powers of observation.

A second journey was to Guatemala. This study of the tropics was botanically profitable, but it impaired his health. By a curious coincidence he passed considerable time in investigating the Flora of a country from which his classmate, Captain Donnell Smith of Baltimore, has obtained such interesting botanical results.

His third journey was to Europe. I had the great pleasure of accompanying him, and of seeing his delight at the gardens of the Old World. But he shrank here, as always, from even the slightest sacrifice of any time for merely social matters. With two exceptions, he declined all the attentions which were tendered him.

Foreign distinctions were beginning to be bestowed upon him in the last years of his life. He had for some time been a highly valued member in our American academies and associations. But distinctions and honors of all kinds were to him almost a matter of indifference. He accepted the honors less for himself than from a regard for the feelings of others. Nothing was more foreign to his nature than any scramble for priority; hence his reclamations are few. He was averse to holding any office; but when he was forced to submit to this infliction, he surrendered at discretion, and performed his duties not only acceptably and faithfully, but gracefully.

No one who came in contact with him could fail to see how warm and deep were his sympathies. The writer had the great privilege of seeing Watson almost every day for about twenty college years, and he can bear willing testimony to the truth of the following words, written by one of the classmates of 1847, Professor Jesup of Dartmouth College: —

"His was one of those true and gentle natures that can always be trusted. He dreaded most of all to be a source of anxiety to his friends, not realizing that a fuller expression of his hopes and fears and plans would often have afforded them vastly more relief than pain. . . . In the family he was self-denying and very thoughtful of the interests of others, doing many a kind act, the recipient of which knowing nothing of the source from which it came. . . . He was a man of decidedly religious character, though he could seldom be induced to take any public part in religious exercises. He was fond of his church, and for years instructed a Bible class.

"He seemed more deeply impressed than almost any one I have ever known, that life is short, and that the field is growing more and more extensive every day. He believed that he must work, while the day lasted and with no reference to any reward except the knowledge that he had done what he could. I doubt whether he ever thought of posthumous fame."

But as we all know, this unsought reward of posthumous fame is his. That it should have come to one who did not fall upon his life work until middle age shows how well that life work was done after it was well in hand. One of his friends has fitly said: "Had he died twenty years after graduation, the world would have known little of him, and his classmates would have considered his life a failure. That long period, however, comprised years of diversified preparation, which enabled him to bring to his chosen task thoroughly trained powers and gave him a range of knowledge drawn from the study of several sciences."

A loyal son of Yale College, he was also devoted to the College of his adoption. Almost his last request was that his remains might be placed in the Harvard University grounds at Mount Auburn. There they rest, near by the tomb of his associate and constant friend, Asa Gray.

The following list of Dr. Watson's papers has been prepared by J. A. Allen, Ph. B., Assistant at the Gray Herbarium, Cambridge.

United States Geological Exploration of the Fortieth Parallel, Clarence King, Geologist in charge. Vol. V. Botany. By Sereno Watson, aided by Prof. Daniel C. Eaton, and others. Illustrated by a map and forty plates. Washington, 1871.

List of Plants collected in Nevada and Utah, 1867-69; numbered as distributed. United States Geological Exploration of the Fortieth Parallel, Clarence King, U. S. Geologist, in charge. Sereno Watson, Collector. Washington, 1871.

Contributions to American Botany. I. New Plants of Northern Arizona and the Region adjacent. American Naturalist, Vol. VII. pp. 299-303, 1873.

Contributions to American Botany. II. Revisions of the extra-tropical North American Species of the Genera Lupinus, Potentilla, and Œnothera. Proc. Amer. Acad., Vol. VIII. pp. 517-618, 1873.

Contributions to American Botany. III. On Section Avicularia of the Genus Polygonum. American Naturalist, Vol. VII. pp. 662-665, 1873.

Note on Chenopodium leptophyllum, Nutt. Bulletin Torrey Botanical Club, Vol. IV. p. 63, 1873.

Contributions to American Botany. IV. Revision of the North American Chenopodiaceæ. Proc. Amer. Acad., Vol. IX. pp. 82-126, 1874.

List of Plants collected in Nevada, Arizona, and Utah, upon Lieut. G. M. Wheeler's Survey, in 1871 and 1872. By Sereno Watson. (In Catalogue of Plants collected in the years 1871, 1872, and 1873, with Descriptions of New Species. Geographical and Geological Explorations

and Surveys West of the One Hundredth Meridian, Lieut. Geo. M. Wheeler in charge. Washington, 1874.)

Contributions to American Botany. V. Revision of the Genus Ceanothus, and Descriptions of New Plants, with a Synopsis of the Western Species of Silene. Proc. Amer. Acad., Vol. X. pp. 333–350, 1875.

Some Notes and Descriptions of New Species, by Sereno Watson, inserted in Botanical Observations in Southern Utah in 1874, by Dr. C. C. Parry. American Naturalist, Vol. IX. pp. 267–273 and 346–351, 1875.

Botany of California. Vol. I. Polypetalæ, by W. H. Brewer and Sereno Watson. Gamopetalæ, by Asa Gray. Cambridge, Mass., 1876.

Contributions to American Botany. VI. 1. On the Flora of Guadalupe Island, Lower California. 2. List of a Collection of Plants from Guadalupe Island, made by Dr. Edward Palmer, with his Notes. 3. Descriptions of New Species of Plants, chiefly Californian, with Revisions of certain Genera. Proc. Amer. Acad., Vol. XI. pp. 105–148, 1876.

Historical Note on Beans. Bulletin Torrey Botanical Club, Vol. VI. p. 104, 1876.

Contributions to American Botany. VII. Descriptions of New Species of Plants, with Revisions of Lychnis, Eriogonum, and Chorizanthe. Proc. Amer. Acad., Vol. XII. pp. 246–278, 1877.

Note on Iris. American Naturalist, Vol. XI. pp. 306–307, 1877.

Bibliographical Index to North American Botany; or Citations of Authorities for all the recorded Indigenous and Naturalized Species of the Flora of North America, with a Chronological Arrangement of the Synonymy. Part I. Polypetalæ. No. 258, Smithsonian Miscellaneous Collections. Washington, 1878.

Contributions to American Botany. VIII. The Poplars of North America. American Journal of Science and Arts, Vol. XV. pp. 135–136, 1878.

Report upon United States Geographical Surveys West of the One Hundredth Meridian, in charge of Lieut. Geo. M. Wheeler. Vol. VI. Reports upon the Botanical Collections made in Portions of Nevada, Utah, California, Colorado, New Mexico, and Arizona, during the years 1871, 1872, 1873, 1874, and 1875. By J. T. Rothrock and others. With thirty plates. The Leguminosæ by Sereno Watson. Washington, 1878.

Review of Gray's Synoptical Flora of North America. American Naturalist, Vol. XII. pp. 686–689, 1878.

Characterized Description of Lilium Parryi, by Sereno Watson; inserted in A New Californian Lily, by Dr. C. C. Parry. With two plates. Proc. Davenport Acad. of Nat. Sciences, Vol. II. pp. 188–189. Davenport, Iowa, 1880.

Contributions to American Botany. IX. 1. Revision of the North American Liliaceæ. 2. Descriptions of some New Species of North American Plants. Proc. Amer. Acad., Vol. XIV. pp. 213–303, 1879.

Botany of California. Vol. II. By Sereno Watson. Cambridge, Mass., 1880.

Contributions to American Botany. X. 1. List of Plants from Southwestern Texas and Northern Mexico, collected chiefly by Dr. E. Palmer in 1879–80. — I. Polypetalæ. 2. Descriptions of New Species of Plants from our Western Territories. Proc. Amer. Acad., Vol. XVII. pp. 316–382, 1882.

Contributions to American Botany. XI. 1. List of Plants from Southwestern Texas and Northern Mexico, collected chiefly by Dr. E. Palmer in 1879–80. — II. Gamopetalæ to Acotyledones. 2. Descriptions of some New Western Species. Proc. Amer. Acad., Vol. XVIII. pp. 96–196, 1883.

Review of Henry John Elwes's Monograph of the Genus Lilium. American Journal of Science and Arts, Vol. XXV. pp. 82–83, 1883.

Manual of the Mosses of North America. By Leo Lesquereux and Thomas P. James. With six plates illustrating the Genera. (Revised before publication by Sereno Watson.) Boston, 1884.

Contributions to American Botany. XII. 1. A History and Revision of the Roses of North America. 2. Descriptions of some New Species of Plants, chiefly from our Western Territories. Proc. Amer. Acad., Vol. XX. pp. 324–378, 1885.

Contributions to American Botany. XIII. 1. List of Plants collected by Dr. Edward Palmer in Southwestern Chihuahua, Mexico, in 1885. 2. Descriptions of New Species of Plants, chiefly from the Pacific States and Chihuahua. 3. Notes upon Plants collected in the Department of Yzabal, Guatemala, February to April, 1885. — I. Ranunculaceæ to Connaraceæ. 4. Notes upon some Palms of Guatemala. Proc. Amer. Acad., Vol. XXI. pp. 414–468, 1886.

Contributions to American Botany. XIV. 1. List of Plants collected by Dr. Edward Palmer in the State of Jalisco, Mexico, in 1886. 2. Descriptions of some New Species of Plants. Proc. Amer. Acad., Vol. XXII. pp. 396–481, 1887.

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A Point in Nomenclature. (Synonymy of Cliftonia nitida, Gærtn. fil.) Bulletin Torrey Botanical Club, Vol. XIV. p. 167, 1887.

Contributions to American Botany. XV. 1. Some New Species of Plants of the United States, with Revisions of Lesquerella (Vesicaria), and of the North American Species of Draba. 2. Some New Species of Mexican Plants, chiefly of Mr. C. G. Pringle's Collection in the Mountains of Chihuahua, in 1887. 3. Descriptions of some Plants of Guatemala. Proc. Amer. Acad., Vol. XXIII. pp. 249–287, 1888.

Notes, and Notices of new or little known Plants Garden and Forest, Vol. I., New York, 1888: —

Iris tenuis, p. 6, fig. 3.
Note on our Native Irises, p. 18.
Lilium Grayi, p. 19, fig. 4.
Aquilegia longissima, p. 31, fig. 6.
Iris bracteata, p. 43, fig. 8.
Phlox adsurgens, p. 66, fig. 11.
Chionophila Jamesii, p. 79, fig. 15.
Cypripedium fasciculatum, p. 90, fig. 16.
Rosa minutifolia, p. 102, fig. 22.
Hymenocallis humilis, p. 114, fig. 23.
Brodiæa Bridgesii, p. 125, fig. 24.
Hymenocallis Palmeri, p. 138, fig. 25.
Rocky Mountain Cypripediums, p. 138.
Delphinium viride, p. 149, fig. 29.
Heliconia Choconiana, p. 161, fig. 31.
Camassia Cusickii, p. 172, fig. 32.
Amelanchier alnifolia, p. 185, fig. 34.
Pitcairnia Jaliscana, p. 195, fig. 35.
Pitcairnia Palmeri, p. 209, fig. 38.
Philadelphus Coulteri, p. 232, fig. 40.
Amelanchier oligocarpa, p. 245, fig. 41.
Phlox Stellaria, p. 256, fig. 42.
Cypripedium Californicum, p. 281, fig. 45.
Erythronium Hendersoni, p. 316, fig. 50.
Tigridia Pringlei, p. 388, fig. 61.
Phlox nana, p. 413, fig. 66.
Hibiscus lasiocarpus, p. 425, fig. 68.
Rosa Nutkana, p. 449, fig. 70.
Berberis Fendleri, p. 460, fig. 72.
Pentstemon rotundifolius, p. 472, fig. 73.
Berberis Fremonti, p. 496, fig. 77.

Note. — Is there a second species of Conradina? Bulletin Torrey Botanical Club, Vol. XV. p. 191, 1888.

An erratum (concerning Cacalia tussilaginoides, HBK.) to Contribution XIV. Botanical Gazette, Vol. XIII. p. 322, 1888.

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Contributions to American Botany. XVI. 1. Upon a Collection of Plants made by Dr. E. Palmer, in 1887, about Guaymas, Mexico, at Muleje and Los Angeles Bay in Lower California, and on the Island of San Pedro Martin in the Gulf of California. 2. Descriptions of some New Species of Plants, chiefly Californian, with Miscellaneous Notes. Proc. Amer. Acad., Vol. XXIV. pp. 36–87, 1889.

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Neillia Torreyi, p. 4, fig. 84.
Rosa humilis, var. triloba, p. 76, fig. 93.
Helianthus mollis, var. cordatus, p. 136, fig. 100.
Calochortus Obispoensis, p. 160, fig. 101.
Portlandia pterosperma, p. 208, fig. 105.
Cordia Greggii, var. Palmeri, p. 233, fig. 106.
Brodiæa Palmeri, p. 244, fig. 107.
Rosa Engelmanni, p. 376, fig. 121.
Tigridia buccifera, p. 412, fig. 125.

Contributions to American Botany. XVII. 1. Miscellaneous Notes upon North American Plants, chiefly of the United States, with Descriptions of New Species. 2. Descriptions of New Species of Plants from Northern Mexico, collected chiefly by Mr. C. G. Pringle, in 1888 and 1889. Proc. Amer. Acad., Vol. XXV. pp. 124–163, 1890.

On the Genus Eriogynia. With plate. Botanical Gazette, Vol. XV. pp. 241–242, 1890.

The Relation of the Mexican Flora to that of the United States. Abstract published in the Proceedings of the American Association for the Advancement of Science, Vol. XXXIX. pp. 291–292, 1890.

Notices of new or little known Plants. Garden and Forest, Vol. III., New York, 1890: —

Rosa foliolosa, p. 100, fig. 22.
Lycoris squamigera, p. 176, fig. 32.
Schubertia grandiflora, Mart. & Zucc., p. 368, fig. 48.

Contributions to American Botany. XVIII. 1. Descriptions of some new North American Species, chiefly of the United States, with a Revision of the American Species of the Genus Erythronium. 2. Descriptions of new Mexican Species, collected chiefly by Mr. C. G. Pringle, in 1889 and 1890. 3. Upon a wild Species of Zea from Mexico. 4. Notes upon a Collection of Plants from the Island of Ascension. Proc. Amer. Acad., Vol. XXVI. pp. 124–163, 1891.

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A New Astragalus. Zoe, Vol. III. p. 52. San Francisco, April, 1892.

On Nomenclature. (In press.) Botanical Gazette, Vol. XVII., June, 1892.

Dr. Watson was engaged at the time of his death in the continuation of the Synoptical Flora of North America.

ASSOCIATE FELLOWS.

GEORGE W. CULLUM.

General George W. Cullum was born in the city of New York on the 25th of February, 1809. While he was quite young his family removed to Meadville, Pennsylvania, where he received an excellent preparatory education which well fitted him for admission to the Military Academy at West Point. He was entered, July 1, 1829, and graduated third in his class of forty-three members, July 1, 1833. He was then promoted in the army to Brevet Second Lieutenant, Corps of Engineers, in which corps he was further promoted to Second Lieutenant, April 20, 1836; Captain, July 7, 1838; Major, August 6, 1861; Lieutenant Colonel, March 3, 1863; and Colonel, March 7, 1867. He was appointed Brigadier General of United States Volunteers, November 1, 1861, and received the brevet rank of Major General, U. S. Army, March 13, 1865, in recognition of his services during the Rebellion. July 13, 1874, he was retired from active service according to law, being over the age of sixty-two years.

General Cullum served actively over forty years as a constructor of military works and light-houses, as commander of Engineer troops, as Instructor and Superintendent of the United States Military Academy at West Point, as Aide de Camp and Chief of Staff to the General in Chief of the Army, and as member of various boards to devise seacoast and other fortifications, river and harbor improvements, etc.

He was distinguished as an author of numerous military, scientific, historical, and biographical works, and was a leading spirit in several scientific societies.

He died of pneumonia at his residence in New York City, on the 28th of February, 1892.

Between the time of his graduation and the breaking out of the Mexican War, he served as Assistant Engineer in the construction of Fort Adams at Newport Harbor, as Superintending Engineer of the construction of Fort Trumbull and Battery Griswold in New London Harbor, and Forts Independence, Warren, and Winthrop in Boston Harbor, of the pier and lighthouse at Goat Island, Newport Harbor, and as Assistant to the Chief Engineer at Washington.

During the Mexican War he was charged with devising and constructing sapper, miner, and ponton trains for our armies, and preparing a text-book on military bridges.

After the war he was placed on duty at the Military Academy as commandant of Sappers, Miners and Pontoniers, Instructor of Practical Military Engineering, etc. Here he remained until 1850, when his health was so broken down that he was compelled to go abroad on a sick leave of absence, which he spent in travelling through Europe, Asia, Africa, and the West Indies. The climate of Egypt completely restored him. In 1852 he resumed his former duties at West Point, and in 1853–54 he also superintended the modification of the Treasury Building in New York City. From 1855 to the breaking out of the Civil War he served as Superintending Engineer of the construction and repair of Fort Sumter, Castle Pinckney, Fort Macon, Fort Caswell, Fort Moultrie, Clark's Point, Fort Adams, Fort Trumbull, Battery Griswold, Willet's Point, and Fort Schuyler, and of the harbor improvements of Charleston. In 1858 he was a member of the Board on the Defences of New York Harbor.

During the Civil War he served as Aide de Camp to General Scott, as Chief Engineer and Chief of Staff of the Department of Missouri and of the Mississippi, and as Chief of Staff of General Halleck, then in command of the Army. In 1861–62 he conducted extensive military operations, more especially of an engineering character. His position as Chief of Staff was one of great responsibility, and afforded him an opportunity to exercise great influence on all the military operations of the war. In addition to these duties, his talents were required in those branches in which he was especially proficient, such as organizing systems of fortification and improving the ponton service, revising the programme of instruction at the Military Academy, etc. In this work he was sometimes associated with other officers, and the reports of the boards upon which he served mark one of the most important eras in the history of modern warfare. These reports were the first to announce and formulate the radical changes that were demanded by the increased power of modern ordnance, and have formed the basis of all subsequent methods that have been adopted by the armies and navies of America and Europe. As General Cullum's talents and tastes rather inclined him to the literary part of the work, he was generally selected to prepare these reports. From 1861 to 1864 he was a member of the United States Sanitary Commission.

In 1864 he was appointed Superintendent of the United States Military Academy. From 1866 to 1868 he was stationed in New York City as a member of the Board of Engineers on New York Harbor, and from 1868 to 1874 as a member of the permanent board, whose duty it was to prepare all schemes of fortification required for the defence of the seacoast of the United States, and to advise the Chief of Engineers on all important points connected with river and harbour improvements. A complete list of his military duties is given in his own Biographical Register, Vol. I. pp. 535–537.

After his retirement from active service, in 1874, he devoted his time to literary work with untiring energy. He has been Vice-President of the American Geographical Society since 1874, and President of the Geographical Library Society of New York since 1880. He was a member of the Board of Managers of the New York Association for the Improvement of the Condition of the Poor from 1880 to 1882; of the Farragut Monument Association from 1880 to 1881; a delegate to the conference of the Association for the Reform and Codification of the Law of Nations, held at Cologne in 1881, and of the International Geographical Conference, held at Venice, September, 1881. He has been a member of the Association of the Graduates of the United States Military Academy since 1870; a Corresponding Member of the Massachusetts Historical Society since 1883; an Associate Member of the American Academy and of the American Historical Association since 1885.

The following extracts from the Bulletin of the American Geographical Society, and from the Annual Report of the Association of the Graduates of the Military Academy, show the high esteem in which he was held by his associates.

"Resolved, that in the death of our first Vice-President, Major General George W. Cullum, U. S. Army, this society has lost one of the most eminent, useful, and devoted of its members. No one who has been connected with it during the forty years of its existence had a more comprehensive view of the importance of the inquiries to which its labors have been directed, or saw more clearly how much it might accomplish for the benefit of mankind, if its resources were adequate to the great field before it. For the seventeen years during which he acted as Vice President, his efforts were untiring to make it what it ought to be, and what he belived it ultimately would become. He took upon himself a large share of those executive labors that are indispensable to the successful management of such an institution, overlooked its extensive correspondence and advised respecting it, gave much of his attention to the publication of the journal, and scarcely a day passed during those seventeen years that he did not come to the Society's house to supervise some matter of detail. The narrow limits of a resolution will not admit of an enumeration of all that he has done for our institution. We can only express our deep sense of our loss, our appreciation of his wide and accurate knowledge, and our high regard for him as a man." *

"General Cullum was a leading spirit in the organization of the Association of Graduates, in 1870. He was its most enthusiastic supporter, and it is safe to say that without his aid and assistance in its management the Association would not have survived the infant stages of its existence and lived to attain such a robust majority. General Cullum prepared more of the obituaries published in our annual reports than any twenty-five other graduates. He was ever ready to respond to a request to write the history of deceased graduates. He became a member of the Executive Committee in 1871, and was the Chairman from 1878 till his death." †

List of General Cullum's Publications.

Military Bridges with India Rubber Pontons, 1849.
Register of the Officers and Graduates of the United States Military Academy, 1850.
Translation of Duparcq's "Elements of Military Art and History," 1863.
Systems of Military Bridges, 1863.
Biographical Register of the Officers and Graduates of the United States Military Academy, 1867, 1879, 1890.
Campaigns and Engineers of the War of 1812-15 against Great Britain.
Struggle for the Hudson during the American Revolution, in the "Narrative and Critical History of America."
Fortification and Defences of Narragansett Bay, 1888.
Feudal Castles of France and Spain.
Numerous contributions to the publications of Societies, etc.

General Cullum's military writings were highly esteemed by those of his own profession, and the translation of Duparcq's "Military Art and History," which was presented in a most attractive form at the time of the Civil War, was eminently useful to the officers of the volunteer army.

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* Bulletin Amer. Geog. Soc., March, 1882.
† Report, Ann. Reunion, 1892.

His historical writings embodied the results of original and exhaustive research in the military history of several campaigns of the Revolution and of the War of 1812. He not only collected all documentary evidence on the subject, but devoted much time to a personal examination of battle fields and sites of ancient defences, and brought the light of his own military study and experience to bear upon the situation. These writings are accordingly of great value to historical and military readers, from the fact that these very fields are more likely than any others to become the theatre of future military operations.

Of all General Cullum's works, his Biographical Register is the most important. General Wright in his obituary notice says: "This work, which in its third edition is extended to include the class which graduated in 1890, is indeed a fitting monument to his memory. While so universally appreciated by the graduates of the Academy, it may be confidently asserted that no other of their number could be found to undertake so herculean a labor, which nothing but his will and untiring energy, combined with his love for the school to which he owes so much, could have carried to a successful conclusion." Every source of information, official and private, was exhausted to make the work accurate and complete; archives were ransacked, tons of manuscript were examined, letters by thousands were written, and almost countless interrogatories were put whenever there was a hope of gleaning any information at all reliable. Although General Cullum was an exceedingly frugal man, he not only defrayed the cost of publishing this work from his private funds, but made in his will a bequest of twenty thousand dollars for its continuance. All future American historians will depend upon it for important data. The Military Academy numbers among its graduates many who have been distinguished in all branches of civil life. The number who have made their impress upon the history of the country, and occupied high positions of trust in political life, or become distinguished as civil engineers or scientists, is hardly realized outside of their own circle. Accordingly, in reading the Register in its final form we follow the thread of American history throughout the nineteenth century.

From his economical habits, General Cullum had amassed a large fortune, which was still further increased by his marriage late in life with the widow of General Halleck, granddaughter of General Alexander Hamilton. Leaving no immediate heirs, he bequeathed the greater part to the institutions in which he had been interested. The most important items were $250,000 for the erection of a Memorial Hall at West Point, stipulating in his will that the sword, bust, and portrait of General Halleck should be deposited there; $20,000 for mural tablets and painted portraits of deceased officers and graduates; $20,000 for the continuance of Cullum's Biographical Register of the Graduates of the Military Academy, to be published decennially; $10,000 to the Association of Graduates of the Academy; and $100,000 for a hall for the American Geographical Society.

From this sketch it appears that, apart from his professional duties, he devoted his whole life to a few great objects. He was deeply impressed with the necessity of thorough military education. He believed that the country had already been saved or benefited in more than one instance by the skill and loyalty of the graduates of West Point, that a complete and unbiased record of their services would be the surest way to establish this belief, and that the certainty of such record in the past and future would also add to the *esprit de corps* and sense of responsibility of all graduates. He had no sympathy for the conduct of the few that joined the Confederate States in the Civil War, but stated the facts in unequivocal terms, and dropped their military record without further comment.

His historical writings were all directed to general questions of the military defence of the country against foreign invasion. His geographical labors absorbed the rest of his available time.

The wealth which economy and other circumstances had placed within his grasp was not squandered in personal indulgence, but reserved for posthumous work, directed to the same general purposes, excepting the portion bequeathed to relatives and friends.

It is not surprising that he appeared cold and undemonstrative to those who were not in perfect sympathy with his work and his method of conducting it. He had a few intimate friends to whom he was steadfastly attached. He was an excellent judge of character, and his criticisms of men and motives were often astonishing in view of the relations into which he had been personally thrown with them. He was interested in humanity at large, and this combined with his wide and varied experience, his general information, his refined manner, and a certain occult sense of humor to make him a very interesting companion.

JOHN C. FREMONT.

It is a singular circumstance in the career of John C. Fremont that his important services as an explorer and his contributions to science were brought to a close when he was scarcely more than thirty-four years of age. He was born in the State of Georgia in the year 1813, and from the year 1842 to the year 1846 inclusive he undertook and carried to a successful result three expeditions from the Mississippi River across the plains, and finally over both chains of the Rocky Mountains, to the Pacific Ocean. Mr. Jefferson, during his administration, had realized the importance of securing "open over-land commercial relations with Asia," as stated in one of his messages to Congress; and, as a preparation for establishing such relations with Asia, he originated and organized the expedition of Lewis and Clarke, whose duty it was to trace the affluents of Columbia River now known as Snake River and Clarke's Fork.

Fremont's early education was obtained under the charge largely of Dr. John Roberton, a Scotchman who had been educated at Edinburgh, and who had established himself at Charleston, S. C., as a teacher of the ancient languages. Dr. Roberton says that in the space of a year Fremont read four books of Cæsar, six books of Virgil, nearly all of Horace, and two books of Livy; and in Greek, all the Græca Minora, about half of the Græca Majora, and four books of Homer's Iliad. At the end of a year he entered the Junior Class of Charleston College, where he gained high standing for study and in scholarship; but for insubordination he was expelled from the College.

In 1833 he was appointed Teacher of Mathematics in the Navy, and made a cruise to South America, which occupied about two and a half years of time. While absent, a law was passed creating the office of Professor of Mathematics in the Navy, for which Fremont upon his return was examined, and appointed. Without entering upon the duties of the place, he declined the position, and accepted the post of Surveyor and Railroad Engineer upon the railway line between Charleston and Augusta. In 1838 and 1839 he was associated with M. Nicollet, a Frenchman and a member of the Academy of Sciences, in an exploring expedition over the Northwestern prairies and along the valley of the Mississippi. During his absence, he was appointed by President Van Buren a Second Lieutenant in the Corps of Topographical Engineers. Upon his return from the Upper Mississippi, and for the period of a year, he was engaged with Nicollet and Mr. Hassler, then the head of the Coast Survey, in the arrangement of the scientific materials that had been collected during the expedition, and in the preparation of a map and a report. In 1842 he was directed by Colonel Abert, the Chief of the Topographical Corps, to make an exploration of the Northwestern frontier of the State of Missouri to the Rocky Mountains, and with special reference to an examination of what was known as the South Pass in those mountains. This expedition was on a small scale, consisting of twenty-one men only, most of whom were of French extraction. In this expedition, he traced the waters of the Platte to the South Pass, which he reached the 8th of August. It was stated by Dr. Linn, then a Senator from the State of Missouri, that "over the whole course of the road barometrical observations were made by Mr. Fremont to ascertain the elevations both of the plains and of the mountains, astronomical observations were made to ascertain latitudes and longitudes, the face of the country was marked as arable or sterile, the facility of travelling and the practicability of routes noted, the grand features of nature described and some represented in drawings, military positions indicated, and a large contribution to geology and botany was made in varieties of plants, flowers, shrubs, trees, and grasses, and rocks and earths, which were enumerated." The second expedition, of May, 1843, was upon a larger scale, and it was not completed until the month of July, 1844. He was directed to extend his survey across the continent, on the line of travel between the State of Missouri and the tide-water region of the Columbia. In its execution, much more ground was covered than had been contemplated in the order. Fremont was the first person that visited the basin of the Great Salt Lake who was able to furnish a scientific and accurate description of the region. Von Humboldt, in his work entitled "Aspects of Nature," (pp. 32-34,) has given a summary of the results reached by Fremont in his first and second expeditions, as follows: —

> "Fremont's map and geographical researches embrace the immense tract of land extending from the confluence of the Kansas River with the Missouri to the cataracts of the Columbia, and the Missions of Santa Barbara and the Pueblo de los Angeles in New California, presenting a space amounting to 28 degrees of longitude (about 1,360 miles) between the 34th and 45th parallels of north latitude. Four hundred points have been hypsometrically determined by barometrical measurements, and for the most part astronomically; so that it has been rendered possible to delineate the profile above the sea's level of a tract of land measuring 3,600 miles, with all its inflections, extending from the north of Kansas to Fort Vancouver and to the coasts of the South Sea (almost 720 miles more than the distance from Madrid to Tobolsk). As I believe I was

the first who attempted to represent, in geognostic profile, the configuration of Mexico and the Cordilleras of South America, — for the half-perspective projections of the Siberian traveller, the Abbé Chappe, (Chappe d'Auteroche, *Voyage en Sibérie, fait en* 1761, 4 vols., 4th ed., Paris, 1768.) were based on mere, and for the most part on very inaccurate, estimates of the falls of rivers, — it has afforded me special satisfaction to there find the graphical method of representing the earth's configuration in a vertical direction, that is, the elevation of solid over fluid parts, achieved on so vast a scale. In the mean latitude of 37° to 43°, the Rocky Mountains present, besides the great snow-crowned summits, whose height may be compared to that of the Peak of Teneriffe, elevated plateaux of an extent scarcely to be met with in any other part of the world, and whose breadth from east to west is almost twice that of the Mexican highlands. From the range of mountains which begin a little westward of Fort Laramie, to the farther side of the Wahsatch Mountains, the elevation of the soil is uninterruptedly maintained from 5,000 to upwards of 7,000 feet above the sea level ; nay, this elevated portion occupies the whole space between the true Rocky Mountains and the Californian snowy coast range from 34° to 45° north latitude. This district, which is a kind of broad longitudinal valley, like that of Lake Titicaca, has been named the *Great Basin* by Joseph Walker and Captain Fremont, travellers well acquainted with those western regions. It is a *terra incognita* of at least 128,000 English square miles, almost uninhabited, and full of salt lakes, the largest of which is 3,940 Parisian (or 4,200 English) feet above the level of the sea, and is connected with the narrow Lake Utah (Fremont, *Report of the Exploring Expedition*, pp. 154 and 273-276), into which the 'Rock River' (*Timpan Ogo* in the Utah language) pours its copious stream."

Fremont's third expedition was commenced, August 16, 1845, under instructions to explore the interior of the region known as the Great Basin, and the maritime parts of Oregon and California. The first important incident of that expedition was the message of General Castro, Governor of California, ordering Fremont to leave the territory. This was in the month of March, 1846. At the moment, Fremont refused to obey the order, and proceeded to fortify his camp, where he raised the United States flag, and remained for about three days. On further consideration, however, he left his camp and proceeded north towards Oregon. In the early part of the month of May he was overtaken by a messenger named Neal, who informed him that Lieutenant Gillespie, an agent of the government at Washington, was on his way, charged with the delivery of letters, and with verbal instructions from the authorities. Upon receipt of this information, Fremont changed his course, and on the second day met Gillespie, who brought only a letter of introduction from the Secretary of State, Mr. Buchanan, with letters and papers from Senator Benton. From Gillespie he learned that it was the purpose of the authorities to ascertain the disposition of the inhabitants of California, to conciliate their feelings in favor of the United States, and to counteract as far as possible any designs of the British government upon that Territory. Fremont made his way to the settled parts of California, near Monterey, where he found Commodore Sloat in command of a United States fleet. In co-operation with him, and largely through Fremont's agency, the Mexican authorities were dispersed, the flag of the United States was raised at Monterey and other points, and all was accomplished before information was received of the existence of war between the United States and Mexico. These proceedings were justified by the government of the United States. In the month of December following, Brigadier General S. W. Kearny arrived in the Territory, and ultimately there was a conflict between him and Commodore Stockton, who had succeeded Commodore Sloat, as to the command of the forces in California. Until the arrival of Kearny, Fremont had been acting under the orders of Commodore Stockton, had raised troops, and had received from him the appointment of Governor of the Territory. General Kearny, in asserting his authority as Commander in Chief, ordered Fremont to raise troops, and to submit himself to his orders. This Fremont declined to do, giving as his reason that he had acted under Commodore Stockton, that it was their duty to adjust their differences, and that until they had done so he should act under the orders of Commodore Stockton. This course on his part led to his arrest while on his way to Washington, and his trial by a court martial upon three charges: "1st, mutiny; 2d, disobedience of orders; and 3d, conduct prejudicial to good order and discipline." On these charges he was convicted, and sentenced by the court martial to be dismissed from the service. Six of the officers who were of the court recommended him to the clemency of the President. The President disapproved of the findings of the court as to the charge of mutiny, but expressed the opinion that the second and third charges were sustained by the proofs; but that, in consideration of the valuable services of Lieutenant Colonel Fremont, the penalty of dismissal from the service was remitted. When the findings of the court were announced, and the action of the President was made known to Fremont, he wrote a letter to the Adjutant General resigning his commission as Lieutenant Colonel in the Army, and giving as a reason that he could not, by accepting the clemency of the President, admit the justice of the sentence.

It is not easy, from a legal point of view, to justify the action of the President. If the conduct of Fremont in refusing to recognize the authority of General Kearny was an offence, it must have rested upon the fact that Kearny exhibited to him evidence which should have satisfied a reasonable person that he had authority from the President to take command of the military forces in California; and if such authority was exhibited to Fremont and he refused obedience, his refusal constituted the crime of mutiny. The other offences charged against Fremont would have followed as a matter of course; but in the absence of proof that he was guilty of mutiny, there was no evidence whatever on which the minor charges could be sustained. Thus ended Fremont's military services and his career as an explorer when he was less than thirty-four years of age.

Fremont's subsequent career may be considered under three heads. First, in business affairs, in which, apparently, he was unsuccessful. Next, he was the first candidate of the Republican party for the office of President of the United States. His acceptance of the nomination, and his letters and statements touching the policy and purposes of the new organization were not merely formal, but they were pronounced declarations in favor of the movement, with clear expressions in harmony with the object of the party, which was the prevention of the extension of slavery in the Territories. Although a Southern man by birth, his devotion to the freedom of the Territories was as ardent as that of Lincoln, or any of the other leaders of the time. Finally, in the Civil War, he made a tender of his services to the government, and as Major General, and in command of the forces in the Department of Missouri, he issued a proclamation of emancipation of the slaves within his jurisdiction. This proclamation was countermanded by the President, and for the sufficient reason that he reserved to himself the absolute control of the question of the abolition of slavery in the seceding States and within the lines of our armies. It cannot be said that Fremont's military career was marked by any signal successes, but there can be no doubt of his ardent devotion to the cause of the country.

THOMAS HILL.

THE father of Thomas Hill was Thomas Hill, who came to this country from England in 1791. He was a Unitarian, and came to America to enjoy larger freedom of thought, speech, and action than was tolerated in Non-conformists at the epoch of the Birmingham riot.

He established himself as a tanner in New Brunswick, N. J., and afterward served for many years as Judge of the Court of Common Pleas. In 1797 he married as a second wife Henrietta Barker, a grand-niece of Rev. Joshua Toulmin (D. D., H. U. 1794), an eminent Unitarian minister. Her father had left England on account of the persecution to which he had been subjected because of his religious faith and his sympathy with Dr. Priestley. Of this marriage, Thomas, the ninth and youngest child, was born, on the 7th of January, 1818. He inherited from his father a robust physical constitution, and mental powers of a high order. His early education was chiefly under the charge of his sisters, who had the sole care of him after his mother's death in 1824. He was an indefatigable reader in his boyhood, and attributed the formation of his scientific tastes to the reading of Franklin's and Erasmus Darwin's works at the age of twelve. The more logical statement would be, that without a native proclivity to science no boy of twelve would read such books. He went to school from his ninth to his twelfth year. His father died in 1828, and, as he left his family with slender provision for their support, Thomas in 1830 was placed as an apprentice in a newspaper office, whence was issued his first literary production in the form of a poetical New Year's Address to the patrons of the paper. In 1833 he was sent for a year and a half to an Academy near Philadelphia, of which his oldest brother was the Principal. He then became an apothecary's apprentice, and remained in that employment more than three years and a half.

Young Hill had from a very early period looked upon the Christian ministry as the only profession which he was willing to choose for his life work; and when his brothers found that this was not a mere boyish fancy, but, so far as it could be, a settled purpose, they did what they could to enable him to realize it. He was already an advanced scholar in mathematics, conversant with the physics and chemistry of the time, and to some degree an adept in botany and zoölogy; but he knew not a word of any language except his own. He commenced his preparation for college in May, 1838, and in August of the following year entered the Freshman Class of Harvard University, having studied first with Rev. Rufus P. Stebbins of Leominster, and then for a few months at the Leicester Academy. He passed his entrance examination with but one condition, and that was in arithmetic, in which he was probably by far his examiner's superior. I think that I know how and why he was thus conditioned. The examination in arithmetic then consisted in the solution of problems, or, to use the vernacular, in doing sums on the spot. With his habit of prompt mental calculation he undoubtedly omitted two thirds of the intermediate steps required by the rules of the arithmetic, and the Tutor condemned his work because he missed in it the processes which a less apt arithmetician would have written out in full. He had become thoroughly grounded in the elements of the Greek and Latin tongues, and was from that time onward an accomplished classical scholar, insomuch that when, during his Presidency at Harvard, he was obliged on one occasion to make a Latin speech of some length, Professor Lane, to whom it was submitted, pronounced it faultless. He held the first place in his class, until during his Junior year he broke down from overwork, and was obliged to leave Cambridge for a while. He always regarded his memory as having been somewhat impaired by that illness; but if so, it must have previously been preternaturally capacious and retentive; for in after years he seemed never at a loss in recalling whatever he had read, heard, or known, even in the minutest details. He graduated the second in his class. In mathematics he had so far distinguished himself that Professor Peirce persistently attempted to dissuade him from the ministry, and to induce him to devote himself entirely to mathematical and physical science. He had also the offer of a high position — the directorship, if I am rightly informed — in the National Observatory at Washington, and he was fully aware of the distinction which he was sure to attain as a man of science; but the profession that he had chosen held at that early time, and held equally to the day of his death, the supreme place in his regard, as a post of duty, of privilege, and of happiness, — a post which he retained in part after he resigned his first pastorate, and which it was his special joy to resume in full after an interval of thirteen years.

While he was in college he invented an instrument for calculating eclipses and occultations, for which he received, in 1843, the Scott Medal of the Franklin Institute. His Commencement oration was on "The Mathematics," and was described at the time as "the most profound of the exercises of the day," and as "characterized by peculiar soundness of thought and rare powers of reflection." He had preached while in college, and had so far anticipated the studies of the Divinity School that, on graduating, he entered the Middle Class. In the autumn of 1845 he was invited to become pastor of the First Church in Waltham, and was ordained for that charge on the 24th of December. Here he passed fourteen years, which he regarded as the happiest of his life. He won not only the confidence and warm affection of those under his immediate charge, but a foremost place in the esteem and honor of the whole community, even of those most widely separated from him by church affinities, — of Romanists as well as of Protestants. He became an active member of the school board, the chairman for the greater part of the time, and was largely instrumental in improving the methods and enhancing the efficiency of the public schools. While he regarded as chimerical, and, were it not so, as eminently undesirable, the (so called) phonographic reform in printed literature, he took the lead in utilizing the phonetic method for the earliest reading lessons of children. Thus, by their being taught to pronounce letters as they sound in words, the time and labor in acquiring the capacity of reading were abridged by more than one half;* while even when a phonetic primer was used, it was found that the child in due time passed from it to an ordinary reading-book almost without consciousness of the change. While in this movement, revolutionary for the earliest stage of school life, and of immeasurable value, he took the initiative, and has been followed by the most intelligent school boards and teachers, he was unrestingly active in the introduction of methods that had been elsewhere found serviceable, and in testing experimentarily modes of teaching that had any just claim to careful trial. Thus under his direction the Waltham schools became model schools, and a centre of educational enlightenment for neighboring communities.

Meanwhile his parochial relations and intercourse were becoming more and more intimate, and were characterized by mutual confidence and affection, so that he was virtually a dearly beloved member of every family in his flock. I have never known a happier pastorate than his, one more fruitful in its best influences, or one which left on either side more enduring and precious memories. It ought not to have been dissolved, and had he not been too ready to yield his own judgment to what was misrepresented to him as a matter of higher obligation, he would probably have died the minister of Waltham.

He was repeatedly solicited to assume other charges. He was strongly urged, under the most promising auspices, to become minister of a church in Cincinnati. He was subsequently asked to take the Presidency of the Meadville Theological School, but declined, in great part, because he was unwilling to leave the regular ministry. In the summer of 1859, he had the Presidency of Antioch College not so much offered to him as forced upon him. The College never had a reason for being, and its pecuniary capital consisted largely in promises that were never fulfilled. It had the disadvantage of being largely supported, befriended, and reputedly managed by strong and good men in New York and Boston, who were too remote from the site of the College to detect shams and subterfuges which from the first boded no good. Thus the man who was the earliest incumbent of the Greek Professorship commenced the study of the Greek Reader after his election, and had just finished it when he entered on his official duties. But Dr. Hill's friend and kinsman (by marriage), Rev. Dr. Bellows, not only had faith in the College, but was enthusiastic in the advocacy of its claims. He rightly imagined that such an institution could have no more precious godsend than a President who was regarded as hardly second to any as a man of science, who held so honored a position as a minister, and who was already distinguished for his educational ability and services. He felt, and contrived to make Dr. Hill feel, that the needs of the growing West demanded such qualifications for the charge of higher seminaries as could be furnished only from among trained educationists who could not accept such places without serious sacrifice. Dr. Hill consciously made a very great sacrifice; but he had reason to expect at least food and clothing for himself and his family. He was shown, not indeed actually invested capital, but pecuniary guarantees that seemed to provide adequately for the salaries and the running expenses of the College. These guarantees proved to be worthless, and he was obliged to devote the time and labor which might have been of unspeakable worth to the College to solicitation for funds to keep the institution alive. He was so far successful, that when he resigned his office, in the summer of 1862, he had secured the payment of all arrears due to the members of his Faculty, but had not reserved for himself more than ten per cent of his own salary, having been obliged to supply the deficit in part by officiating on Sundays in a Cincinnati pulpit, at a distance of more than seventy miles from the College. Meanwhile, his over-strong sense of obligation made him unwilling to shorten the three years for which he had pledged himself to serve, though within that period he might have had a situation which, if unencumbered, he would gladly have accepted. Among the most influential proprietors of King's Chapel were several men who had been his summer parishioners at Waltham, and they earnestly besought him to suffer his name to be presented for the then vacant pastorate of the Chapel, with the assurance that there would be a unanimous vote in his favor. But this was early in his Presidency. Meanwhile his pecuniary straits were not his only trial. There were jealousies on the part of the (so called) Christian denomination, whose members, though contributing a very small portion of the funds given or promised, claimed a large share in the administration of the College, and possessed neither experience nor skill for such service. On the whole, the best that could have been done, and that only by a man of surpassing prudence, wisdom, and unselfishness, was to come forth from this ordeal with the consciousness of leaving the College in no worse a condition than that in which he found it, and with abounding gratitude, respect, and honor from those associated with him in its administration.

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* The child can perceive no reason why *aitch-o-jee* should spell *hog*, or why *see-you-bee* should spell *cub*. Each separate word is acquired by a separate act of memory; while if he is taught to pronounce each letter as it sounds in the words in which it is used, the rapid pronunciation of the letters of a word gives him the word.

At the time of his resignation the Presidency of Harvard University was vacant, and while Dr. Hill was from the first the favorite candidate of the late John A. Lowell, the senior and by virtue of his experience and practical wisdom the controlling member of the Corporation, the election of Dr. Hill to that office seemed to all the friends of the College the best possible choice ; and there probably never was a case in which the action of the governing boards was more fully and warmly sanctioned by all whom it concerned. While he had the respect and confidence of the entire Faculty, the scientific teachers recognized in him their rightful head, and those in other departments found him no less conversant with their respective lines of work than if they had been his specialties. He already had in the board of instruction many friends, and there were none of the others whom he did not make his friends, while he was singularly fortunate in the appointments voted by his recommendation. He commenced several of the improvements in the administration which — essential to the well-being of the College — it required the vigorous executive capacity of his successor to sustain and carry forward, while they were still regarded in some influential quarters with doubt and dread. The elective system had under him its hopeful beginnings. The Academic Council, which now seems a necessity, was started at his suggestion. Previously the several Faculties of the University, though with many common interests, were without means or opportunity of intercommunication. He originated the system by which they are made one body, with officers, records, and stated times of meetings, for the discussion and elaboration of the various measures by which they may aid one another's efficiency, act concurrently for the benefit of the University as a whole, and provide for the instruction and discipline of those classes of special and graduate students that do not belong exclusively to any one department. Under him, also, University Lectures were first opened to the outside public, — a system which has since been so extended that during each academic year there are a considerable number of courses and of individual lectures in Sanders Theatre and in Sever Hall, which, while primarily for the benefit of students, are also designed and adapted for the receptivity of an intelligent audience from the community at large. It was Dr. Hill's misfortune, that while his heart was in his work, and he was enabled to put into it the results of mature experience and wisdom, he was unavoidably prevented from giving to it the full and uninterrupted stress of vigilance and energy which such an office demands. To the weariness of his Antioch life was added a series of domestic afflictions, under the accumulated pressure of which he was led to resign his charge in the autumn of 1868. He then removed to Waltham, which was his home for the next four or five years. He was for several months too much enfeebled for any intellectual labor, but gradually recovered his strength for nearly twenty years of full vigor of mind, and of working power more intense and fruitful than at any earlier period. In the autumn of 1869 he went to California by the then newly opened Union Pacific Railroad, and, while he gained strength by travel, he also found access to fields and objects of scientific and sociological interest which had not yet become familiar to the New England mind. In 1871 he represented the town of Waltham in the Legislature. In December of that year he sailed with his friend Agassiz on his well known South American expedition, and bore no small part in the explorations which have given it a permanent place in the history of science.

Early in 1873 Dr. Hill was invited to preach in the First Church of Portland, Maine, and immediately received an invitation to its then vacant pastorate, which he accepted, and which he held for the remainder of his life. Here he found himself in a congenial atmosphere, with many of his stated hearers who appreciated the high intellectual standard no less than the spiritual depth of his discourses, and in a community comprising not a few persons of advanced culture in the various departments in which they recognized him as a leading mind. He made himself felt as an educationist on the school board of the city, and the teachers enjoyed his counsel and sympathy. He was an active member of the Portland Natural History Society, and of other local associations scientific and literary. He became largely known in nearer and remoter regions of his adopted State, and his services were solicited on very numerous occasions of public interest. In Portland he was honored, revered, and beloved by the whole community, and had no more genuine admirers and warmer friends in his own church than among the ministers and in the churches most widely separated from him in creed and in modes of worship.

For several years Dr. Hill had delivered in the spring or early summer a course of lectures at Meadville, before the students in the Divinity School. In May, 1891, though but partially recovered from serious illness, he started on a journey in which he visited friends in Ohio, and fulfilled his Meadville engagement on his return. He arrived at Meadville greatly enfeebled, yet could not be dissuaded from delivering his lectures, though the effort so far exhausted him as to make his friends very apprehensive as to his homeward journey. On the 7th of June he reached his daughter's house in Waltham, too ill to go farther, and for several weeks was confined almost wholly to his bed; and there seemed little hope that he would ever leave his room. Here he had the assiduous and skilful care of his son in law, Alfred Worcester, M. D., and after a few weeks the worst symptoms nearly disappeared, and he made arrangements for returning to Portland to take part in the ordination of his colleague, Rev. John C. Perkins. But on the day before that appointed for his departure a relapse occurred, and it became certain that the end was drawing near. After several weeks of severe suffering he died, on the 21st of November, 1891. During this long illness he manifested in full the strength and the sweetness of his character. His courage, patience, and resignation indicated at once perfect self-control and the power of a religious faith which seemed hardly less than a clear vision of things divine and eternal. He was at the same time thoughtful of the comfort of those around him, and of whatever concerned his friends and his official charge in Portland; and there were constantly going out from his chamber by letter and message offices of love and kindness for an extended circle of those whom he had made his own by ties of benefit conferred. While fully prepared to die, he was during intervals of relief hopeful of continued life, that he might avail himself of the diminished stress of professional duty for literary labors in behalf of the interests of science and religion, in his mind joint and inseparable.

Dr. Hill was married in 1845 to Anne Foster Bellows, daughter of Josiah and Mary (Sparhawk) Bellows, of Walpole, N. H., a woman of rare beauty and loveliness of character, of superior ability and culture, and unsurpassed in all that made her precious as a wife and mother. She died in 1864, leaving for her husband the domestic cares and responsibilities of which she had hardly let him feel the pressure. In 1866 he married Lucy Elizabeth Shepard, daughter of Otis and

Ann (Pope) Shepard, of Dorchester. In this new relation there was every promise of happiness for him and for his children; but she early became an invalid, and died in 1869.

Dr. Hill's sons are Henry Barker (H. U. 1869), Professor of Chemistry in Harvard University; Thomas Roby, in business in Philadelphia; and Otis Shepard, only child of his second marriage. Of his four daughters three are married, respectively, to Lewis Pierce (Bowdoin College, 1852, LL. B., H. U. 1855), of Portland, Alfred Worcester (H. U. 1878), M. D., of Waltham, and Robert H. Monks.

Dr. Hill was, in a certain sense, unique, — the only man of his kind that I have ever known. There was, perhaps, no department except mathematics in which he had not his superiors, and there are men who have covered superficially as wide a range of science and knowledge as was within his scope; but the omniscience which was said to be Lord Brougham's foible was his special gift. He not only knew something in every department, but there was none within his reach in which he was not so conversant with principles, truths, and facts that he seemed the peer of an adept, and amply qualified to be a teacher and guide. While as a mathematician he was well known as second to no man of his time, there might be named several other departments in either of which, had it been his specialty, he would equally have held an unrivalled eminence.

In mathematics his earliest publication was an " Elementary Treatise on Arithmetic," designed for pupils of an advanced grade, as an introduction to Professor Peirce's series of text-books. This appeared in 1845. In 1850 he published an " Elementary Treatise on Curvature," and a " Fragmentary Essay on Curves." These works marked the early stages of a series of investigations on curves, in which he performed no small amount of original work, the results of which are somewhat densely strewn in successive records of proceedings of scientific bodies. His attention was specially directed to the curves of nature, those that are found in the various forms of organic life, all of which he believed to be capable of expression by equations in the terms of their co-ordinates, and for not a few of which he determined the equation. In one of the papers to which we refer he described and defined an entirely new curve to which he gave the name of the " Tantalus."

In 1855 he published his " First Lessons in Geometry," followed shortly afterward by a " Second Book." The first of these was designed to create in the child an interest in form and figure by appealing to the imagination, and it made him acquainted by the eye with a very considerable variety of natural curves; while in the second, mathematical reasoning was employed, not only for the demonstration of elementary theorems, but for the solution of problems, some of them such as are usually reserved for a later period of school or even college life, but which he so simplified as to bring them within the comprehension of pupils of tender years. In 1849 he published "Geometry and Faith," in which he exhibited in their close mutual relations, or rather in their identity, the fundamental principles of mathematics and of Christian theism. His sense of the primacy of mathematics among the sciences found expression in his Phi Beta Kappa oration on "Liberal Education," in 1858, and again in a course of Lowell Lectures on "The Mutual Relation of the Sciences," in 1859. After his removal to Portland he invented an instrument to which he gave the name of "Nautrigon," for solving spherical triangles by construction. By its use there would have been a considerable saving of time in nautical calculations; but it was too expensive to come into general use. I have already referred to his early reputation in practical astronomy, in which he was probably as well versed as he could have been, unless he had been directly concerned in the management of an observatory. In physics he was not only familiar with the labors of others, but made independent investigations of no little importance and value. He kept even pace with chemistry in the successive stages of its rapid progress, and would have found himself at home in a laboratory furnished with the latest apparatus. He was conversant with the entire realm of organic life. In zoölogy he was closely associated with Agassiz in his researches, and was constantly engaged in independent observations of the phenomena of animal life, in which Science was indebted to him for not a few discoveries. Botany was, next to pure mathematics, his favorite science, to which he made frequent contributions. He was an intimate friend of Dr. Gray, and a scientific communication was forwarded in a letter to Professor Goodale but a few weeks before his death.

I have spoken of his lifelong interest in classical literature, of which he was, if not a close student, a critical and discriminating reader. He was a good Hebrew scholar, and was not unacquainted with other Semitic languages.

As to the studies specially appertaining to the clerical profession he was among the most learned of our clergy. In the criticism of the Hebrew and Christian Scriptures he was thoroughly trained and skilled. A course of Lowell Lectures on the "Natural Sources of Theology," delivered in 1870, reproduced and greatly enlarged in a series of articles in the "Bibliotheca Sacra," formed the substance of a volume issued in 1877, which is unsurpassed in the clearness, fulness, and timeliness of its statement of the fundamental truths of natural religion, and in its treatment of the various current forms of scepticism.

While Dr. Hill was master of a prose style at once elegant, perspicuous, and strong, his genuine poetic temperament found occasional expression in verse, which, although it gave him no special distinction as a poet, showed that, had he sought a place in the upper region of Parnassus, he could have easily won it. His two volumes of poems are real poetry, equally in conception, diction, and rhythm, and indicate a man of genius as their author.

He was a lover of music, and made earnest endeavors to supply the lack of a discriminating ear. He studied thoroughly the mathematical laws of music, the principles of harmony, and the system of musical notation, and even made some attempts at composition. In the arts of design he had capacity which by cultivation might have become talent, perhaps genius. He painted landscapes in oil which were no mean copies of nature, and was not unsuccessful in modelling portraits in bas-relief.

As to Dr. Hill's personal character the only difficulty in portraying it is that one knows not where to paint in the shadings. Transparently frank, guileless, unsparingly faithful in duty, in all domestic and social relations forgetful only of his own comfort and advantage, and assuming as if rightfully his own every burden that others would let him bear, he manifested in his whole life the beauty and power of the religion of which he was the earnest and devoted minister. He can have had no enemies, but more friends than can be catalogued. Had there been in him aught of self-seeking, he would have left more numerous and permanent records of the reputation in which he is held by all who knew him. In the periodicals to which he was a constant contributor, especially in the "Bibliotheca Sacra" and the "Andover Review," are papers which, if collected and skilfully edited, would form a series of volumes on subjects of vital interest, in which his aim was never to draw attention to himself, but only to instruct and impress the minds and souls of his readers. With like unselfishness of purpose, he was always ready to give aid, at whatever cost of time and labor, to those who were engaged in literary, scientific, or professional work, whether for their own benefit or for publication; and there are not a few reputations greatly enhanced and enriched by contributions from his own best thought and most recondite investigations. In fine, his ruling purpose was to serve every cause of learning, virtue, and religion, and no man cared less than he, if the service were only rendered, whether it was in his own name or in that of others.

As to College honors, Dr. Hill received the degree of Doctor of Divinity from Harvard University in 1860, and that of Doctor of Laws from Yale College in 1863. He was a member of the American Philosophical Society, of the Massachusetts Historical Society, and of many other associations of like character.

The following is a partial list of Dr. Hill's publications in other than pamphlet form: —

Elementary Treatise on Arithmetic, 1845.
Geometry and Faith, 1849. 2d edition, revised and enlarged, 1874. 3d edition, greatly enlarged, 1882.
First Lessons in Geometry, 1855.
Jesus the Interpreter of Nature, and other Sermons, 1860.
Second Book in Geometry, 1863.
Natural Sources of Theology, reprinted from the Bibliotheca Sacra, 1874.
Arithmetic (Wentworth and Hill), 1883.
In the Woods and Elsewhere, 1888.

JOSEPH LEIDY.

Joseph Leidy, a member of this Academy since May 30, 1848, died, after a brief illness, at his residence in Philadelphia, Pa., on April 30, 1891. His ancestors were of French-German descent, and came to this country as missionaries. His father, Philip Leidy, was born in Montgomery Co., Pa., in 1791, and married Catherine Melick.

Joseph Leidy was the third child by this marriage, and was born in Philadelphia, September 9, 1823. His mother died when he was a year and a half old; later his father married Christiana Melick, a sister of his first wife. She proved to be an admirable mother to Joseph, and to her watchful care and direction is due in great measure his choice of life work. His early education was obtained in private schools, and even during this period he manifested a marked inclination toward the study of natural history, being particularly interested in plants and minerals. After hearing a lecture on these subjects, given by an itinerant lecturer in the schoolhouse, young Leidy procured text-books, and began the systematic study of botany and mineralogy. From an early age he showed great skill in drawing. This power became so marked that at the age of sixteen his father removed him from school with the intention of having him become an artist. At this period he spent much of his time in a wholesale drug-store near his home; here he made such good use of the opportunity for studying the nature of various drugs, and in compounding medicines, that the proprietor recommended the boy as being competent to take charge temporarily of the retail drug-store of a customer.

This success led him to consider seriously the advisability of becoming an apothecary. All this time he had continued his natural history studies, and by the dissection of a few cats, chickens, etc., he developed such an interest in comparative anatomy that his step-mother decided that Joseph should become neither an artist nor a druggist, but a physician. Having decided upon the study of medicine, he gave his first year to the study of practical anatomy, and under the preceptorship of Doctors Paul B. Goddard and James McClintock took three full courses of medical lectures at the University of Pennsylvania, receiving in the spring of 1844 the degree of Doctor of Medicine, his thesis being an admirable essay on "The Comparative Anatomy of the Eye of Vertebrated Animals." He now entered upon the active practice of medicine, and at the same time was appointed Assistant to the Chair of Chemistry in the University. He also assisted Dr. Goddard, the Demonstrator of Anatomy.

At the end of two years he gave up the practice of medicine in order that he might devote himself entirely to study and teaching. His skill in anatomy was so great that he was appointed Prosector to the Chair of Anatomy by Professor Horner. In 1846 he was elected Demonstrator of Anatomy in the Franklin Medical College, which position he held for one year and then resigned to return to the University, where he was again associated with Professor Horner. He also gave private courses in anatomy. In the spring of 1848 he accompanied Dr. Horner to Europe, in the fall gave a course of lectures on Histology, and in the following spring lectured on Physiology at the Medical Institute. This constant application affected his health so that he was obliged to abandon all work for some months. In 1850 he went abroad with Dr. George B. Wood to make a collection of models, drawings, etc., with which to illustrate Dr. Wood's course of lectures on Medicine. This trip was of very great value to Dr. Leidy, as it enabled him to visit all the great museums of Europe, and to make the acquaintance of such distinguished anatomists and physiologists as Owen, Majendie, Hyrtl, Johannes Müller, and others. He returned from this trip with renewed health, and in 1851 resumed his anatomical work at the University.

During this year he was elected a member of the College of Physicians and appointed Pathologist to St. Joseph's Hospital. In the winter of 1852 Professor Horner through ill health was unable to continue his lectures on anatomy, and at his request Dr. Leidy was appointed as his substitute. After the death of Dr. Horner, he was, in May, 1858, appointed Professor of Anatomy, which position he held until his death.

During the ten years preceding his appointment to the Chair of Anatomy, in addition to his regular duties, Dr. Leidy found time to continue his scientific studies. In 1844, the year of his graduation, he contributed to Amos Binney's monograph of the Mollusca an admirable introductory chapter on the "Special Anatomy of the Terrestrial Mollusks of the United States," together with sixteen beautifully executed plates illustrating the anatomy of thirty-eight species of Mollusca. In 1845 he was elected a member of the Boston Society of Natural History, and of the Philadelphia Academy of Natural Sciences. With the latter institution he was constantly associated during the rest of his life, being successively Librarian, a Curator, and from 1847 chairman of the Board of Curators. With his natural modesty, he many times refused the office of President, but finally in 1881 accepted it, and remained President of the Academy to the end of his life.

The Proceedings of the Academy furnish a brilliant memorial of his great attainments in various branches of natural science, as they contain several hundred valuable contributions to zoölogy, paleontology, comparative, human, and microscopic anatomy, botany, and mineralogy. While he never regarded himself as an authority, and published but little upon mineralogy and botany, his knowledge of these subjects was that of a specialist. This was well shown by the frequent verbal communications which he made as Curator in calling the attention of the Academy to additions to the mineralogical cabinet; his knowledge of gems and their values was also very extensive. The very fine and valuable mineralogical collection made by him has recently been purchased by the government, and will be placed in the National Museum in Washington.

His familiarity with plants was also frequently noted at the meetings of the Academy and elsewhere. The herbarium which he gave the Biological Department of the University of Pennsylvania contains over 1,500 species which were collected and determined by himself.

In zoölogy he gave especial attention to invertebrate forms; and while paying particular attention to parasites and Protozoa, he made valuable contributions to our knowledge of many other groups. As early as 1846 he observed minute specks in some pork that had been cooked, which, when examined with a microscope, were found to be a species of *Trichina*. In his communication on this discovery he stated that this species was apparently the same as that found by Owen and himself in man. The famous zoölogist Leuckart, who afterward worked out the life history of *Trichina spiralis*, acknowledged his indebtedness to this observation of Dr. Leidy. In 1853 appeared the "Fauna and Flora within Living Animals," a beautifully illustrated and valuable work, which showed very clearly the wide range of animal and vegetable parasites which are to be found in the alimentary canals of small animals, as beetles, centipedes, cockroaches, etc. This paper is also interesting as having expressed ideas closely resembling in many respects those advanced a few years later by Darwin in his "Origin of Species."

Dr. Leidy's contributions to helminthology were numerous, and of such merit as to render him the highest authority on this subject in this country, and the peer of such men as Leuckart, Cobbald, and Diesing. His papers upon various insects and their life histories gave evidence of his familiarity with entomology. In 1848 he made the discovery of the presence of eyes in a species of *Balanus*, which led Darwin to look for them in other members of this group.

Dr. Leidy was particularly interested in the very lowest forms of animal life. In addition to many smaller papers, he gathered together in the magnificent monograph, "Fresh Water Rhizopods of North America," the results of many years' study. The numerous plates illustrating this volume are splendid examples of his marvellous artistic skill. Among the first persons in this country to use the microscope, he early established his ability as a histologist by his valuable paper, "Researches into the Comparative Structure of the Liver" (1848). The views advanced in this paper, though not generally accepted at the time, have since been largely confirmed by embryological research.

In 1861, he published "An Elementary Text-book on Human Anatomy," in which the noteworthy attempt was made to substitute an English terminology with foot-note references for the cumbersome and perplexing anatomical nomenclature in common use. This was quite successful, and was carried to still greater perfection in the second edition of this book, which was finished a short time before his death. This anatomy is unexcelled by any in the language for accuracy of detail and clearness of expression. Dr. Leidy's other papers upon vertebrate anatomy exhibit the careful work and clear judgment so characteristic of all that he did, and the many new facts presented by him have been almost always confirmed by later investigators. No one was more ready than himself to acknowledge and correct an error when found.

There remains still another field of scientific research in which Dr. Leidy achieved a world-wide reputation, namely, paleontology. His first paper on this subject appeared in 1847, "The Fossil Horse of America." Although he was almost the first person in this country to take up the subject of vertebrate paleontology, and had at first very meagre opportunities for the study of the comparative osteology of many recent forms, he produced in the next few years a series of brilliant papers, which entitle him to be considered as the equal of any paleontologist produced by this country or Europe.

The following are among the more prominent of his many contributions to this subject: "Ancient Fauna of Nebraska," 1853; "Memoir of the Extinct Sloth Tribe of North America," 1855; "Cretaceous Reptiles of the United States," 1865; "Extinct Mammalian Fauna of Dakota and Nebraska, together with a Synopsis of the Mammalian Remains of North America," 1869; "Contributions to the Extinct Vertebrate Fauna of the Western Territories," 1873; "Description of Vertebrate Remains from the Phosphate Beds of South Carolina," 1877.

The interest aroused by these wonderful discoveries led others to enter this field of investigation. Great rivalry and many acrimonious disputes regarding priority and nomenclature arose, so that, rather than become entangled in controversy, Dr. Leidy gave up this work in which he had achieved such success, and devoted himself to other fields of scientific work. He however contributed from time to time small paleontological papers, the last appearing in May, 1890.

Dr. Leidy acted as surgeon to the Satterlee Military Hospital during the war, and the results of the many interesting autopsies made by him are recorded in the "Medical and Surgical History of the War."

He was elected a member of the National Academy of Science, in 1863, at the time of its organization. In 1871 he was appointed Professor of Natural History in Swarthmore College; and in 1884, upon the establishment of the Biological Department of the University of Pennsylvania, he was appointed Professor of Zoölogy and Comparative Anatomy. In 1885 he was elected President of the Wagner Free Institute of Science in Philadelphia; and in 1889, at the time of its organization, President of the Association of American Anatomists.

Many honors, both at home and abroad, were conferred upon this distinguished naturalist. In 1886 Harvard University conferred upon him the degree of Doctor of Laws. The Boston Society of Natural History awarded to him, in 1879, the Walker grand prize of $500, which in this instance was raised to $1,000 as a special recognition of his contributions to science. In 1879 he received a prize from the Royal Microscopical Society. The Geological Society of London awarded to him, in 1884, the Sir Charles Lyell medal for his paleontological researches; and in 1888 he received from the Paris Academy of Sciences the Cuvier medal for his work in biology. In the period from 1845 to 1887 he was elected honorary member by over forty of the learned societies of Europe and this country.

It is impossible in this brief notice to do more than indicate in the most general manner the life work of this great man, which covers almost a half-century. In this period his contributions to natural history number nearly one thousand, ranging from short papers to large illustrated volumes, which probably contain fewer errors of fact and interpretation than those of any other writer on so many and such varied subjects. His personal character was in perfect accord with his wonderful mental attainments. He was remarkable for an entire absence of self-assertion or conceit. Wholly unselfish, his amiability and charming simplicity of manner rendered him a delightful companion, always approachable and ready to aid a student by advice or explanation. In the lecture-room his clear and concise descriptions formed word pictures rivalling in distinctness his admirable blackboard illustrations. He was as incapable of deceit as he was modest, and submitted to imposition rather than enter into controversy. His long life was devoted to science for the advancement of knowledge, and without thought of gain or personal glory.

Notwithstanding failing health during the last few months, Dr. Leidy still continued his active work; and thus, as he desired, with his shoulder to the wheel, one of America's greatest naturalists passed away.

NOAH PORTER.

Noah Porter, son of Rev. Noah Porter, D. D. (Yale College, 1803), was born in Farmington, Conn., on the 14th of December, 1811. His father was pastor of the Congregational Church in that town for nearly sixty years, and had high reputation as a learned, wise, faithful, and efficient minister. The son graduated at Yale College in 1831, and immediately took charge of the Hopkins Grammar School in New Haven, — a position which at the end of two years he exchanged for a tutorship in College, at the same time entering the Divinity School. He resigned the tutorship in 1835, and on completing his theological course was ordained, April 27, 1836, as pastor of the Congregational Church in New Milford, Conn. On the 13th of the same month he married Mary Taylor, the eldest daughter of his predecessor, and the sister of Rev. Dr. Taylor, — well known in his time as the advocate of the more liberal type of Calvinism in the Taylor-and-Tyler controversy, — who, as Professor of Divinity, had been his favorite teacher, and may have borne no small part in determining the trend of his pupil's opinions.

Mr. Porter was regarded from the first as a man of superior ability, and his success in a long established church pointed to him as eminently fitted to take charge of a church that had yet to create its own future. He accordingly was invited to the pastorate of the then new (South) Congregational Church of Springfield, Mass., over which he was installed, January 12, 1843. But the friends of the College were undoubtedly right in believing that his special fitnesses were for academic service. He had been devoted to philosophical studies from his college days, and had shown his teaching power and administrative ability in his tutorship; and when a new Professorship of Moral Philosophy and Metaphysics was established, he was at once sought as its incumbent. He was elected to this office in 1846, and filled it with distinction, honor, and growing influence till his death. Still retaining it, though of course delegating much of its work to other hands, he accepted the Presidency of the College on President Woolsey's resignation in 1871, fulfilled the difficult task of maintaining the prestige given it by his predecessor, and retired from the chair while, with unimpaired vigor of mind, his advanced years seemed the only reason for so doing. He, however, was probably conscious of declining bodily strength, and his last years were a period of gradual enfeeblement, followed by an illness of several weeks, which had its fatal issue on the 4th of March, 1892.

President Porter was a voluminous writer. Among his published volumes are "The Human Intellect" (1868); "The American Colleges and the American Public" (1870); "Books and Reading" (1871); "Elements of Intellectual Science" (1872); "Elements of Moral Science" (1885); "Kant's Ethics" (1886); and "Fifteen Years in the Chapel of Yale College" (1887). He also published a large number of sermons, addresses, and articles in periodicals, especially in the New Englander, and was editor in chief of the successive editions of Webster's Dictionary from 1860.

His claims to distinction must have been recognized in more seminaries of learning than he knew. His text-books have had, and still have, a largely extended use in colleges and academies. The degree of Doctor of Divinity was conferred on him by the University of New York in 1858, and that of Doctor of Laws by Western Reserve College in 1870, by Trinity College in 1871, and by the University of Edinburgh in 1886. His was a not infrequent and an always welcome presence at Harvard College, where he is gratefully remembered as a Phi Beta Kappa orator and as a preacher in Appleton Chapel.

President Porter was in every respect a man of high tone, large-hearted, broad-minded, true, sincere, faithful, honorable, making himself not only respected but beloved, and most by those who knew him best. He was a firm Christian believer, with fixed opinions based on deliberate conviction, but with only the kindest regard for those who differed from him. He cannot but have endeared himself to his students by a gentleness which was never weak and a firmness which was never harsh or stern. His text-books are conservative in their philosophy, and especially valuable for the justice and candor with which he treats the various schools and types of speculation, even when most remote from his own. As a preacher he was always instructive and impressive; for his sermons were full of profound thought on subjects of infinite moment, and his style, while massive and with little ornament, was marked by purity of diction, clearness of meaning, and precision of statement. In his early ministry he must have been a popular preacher, in the better sense of the term; of late years he has commanded close attention and deep interest in proportion to the receptivity of his hearers, and their own nearness to his own elevated plane of mind, heart, and soul.

FOREIGN HONORARY MEMBERS.

JOHN COUCH ADAMS.

John Couch Adams was born at Lidcot, England, on June 5, 1819. His unusual mathematical abilities became evident early in his life, and obtained for him the highest honors at the University of Cambridge, where he graduated as Senior Wrangler in 1843. His election to college fellowships made it practicable for him to devote himself to his favorite mathematical pursuits, and in 1858 he was made Professor of Mathematics at the University of St.Andrews in Scotland. He held this position only for a year, as in 1859 he was appointed to a Cambridge Professorship, and accordingly returned to his former residence. In 1861 he succeeded Professor Challis as Director of the Cambridge Observatory, and continued in that office until his death, on January 21, 1892, after a protracted illness. In 1881, he was offered the position of Astronomer Royal, left vacant by Airy's retirement; but advancing years made him unwilling to accept a place requiring so much exertion from its occupant.

The life of Adams, thus outwardly uneventful, practically consisted of a series of mathematical researches. It may be said to have opened with one which had the quality, rare in such work, of attracting public attention by its dramatic character. Immediately after his graduation, he directed his thoughts to the subject, then ripe for consideration, of the unexplained irregularities in the movements of Uranus, and to the question whether the place of an unknown planet, capable of producing such perturbations, could be defined by calculation. In 1845 his solution of the problem was communicated to Challis and to Airy, the Directors of the Cambridge and Greenwich Observatories; but partly through accident, partly through the adoption of too mechanical methods in such search as was undertaken for the theoretical planet in England, the discovery of the actual planet Neptune was reserved for the continent of Europe, where Leverrier furnished the prediction verified by Galle. The similarity of the results independently attained by Adams and by Leverrier was such as to exclude, at least to the uninstructed mind, the possibility that either of the investigators could have erred in his method of inquiry; and the remarkable nature of their achievement won for them general admiration and applause. The theoretical planet which they had discovered by inference certainly differed in many important respects from the observed planet found by Galle. Whether the approximate coincidence of the apparent place among the stars occupied in 1846 by the theoretical and real objects was casual or not, this certainly formed a question to be considered only by men who felt themselves able to compete mathematically with Adams; and it has never been minutely considered by a sufficient number of such men to establish a decision upon the subject from which no appeal can be taken. But in the absence of a clear decision to the contrary, the scientific world continues to regard the predictions of Adams and Leverrier as a real mathematical discovery; while in any case there can be no doubt of the evidence of mental power displayed in the researches from which these predictions resulted, or of their deserved prominence in the history of astronomy.

Among the various researches which were subsequently undertaken by Adams, that relating to the secular variation of the Moon's mean motion was perhaps the most interesting and important. This investigation reopened a question which had been regarded as finally settled by Laplace. Adams detected an omission in the work of his predecessor, which, when supplied, proved to disturb the agreement previously supposed to exist between theory and observation. A new physical cause was now required to explain the observed results, and this was found in the retardation of the rotation of the Earth due to the tides. In this case, a protracted discussion of the subject among the foremost mathematicians who concerned themselves with astronomical inquiries resulted in confirming the theory maintained by Adams. But the amount of the secular variation forming the original subject of discussion has not yet been definitely fixed by observation. At present it seems probable that the researches of Adams brought theory into better accordance with fact, instead of disturbing an existing agreement. If this view should prevail, tidal retardation must be regarded as compensated by terrestrial contraction, or by causes as yet unknown.

The orbit of the remarkable body of meteors to which is due the recurrence of brilliant displays of shooting stars about the middle of November, three times in each century, was another subject investigated by Adams with great success. In general, it may be said that in all the principal discussions of his time respecting recondite questions of theoretical astronomy he took a prominent part, and that no arguments were regarded with more respect than his by those capable of appreciating them.

Besides his academical honors, he received many tokens of distinction from learned societies, and his name was familiar, as it will long continue to be, wherever the mechanism of the solar system is discussed or studied.

GEORGE BIDDELL AIRY.

George Biddell Airy was born at Alnwick, England, July 27, 1801. His university education was obtained at Cambridge, where his mathematical ability became conspicuous, and where he graduated as Senior Wrangler in 1823. In the following year he was elected a Fellow of Trinity College; in 1826 he was made a Professor, and in 1828 the Director of the Observatory. These early honors were abundantly justified by the number and excellence of the investigations which he began even before his graduation, and continued during the following years.

The results of his inquiries at this period were published in the Transactions of the Cambridge Philosophical Society, in memoirs relating to optical and astronomical subjects. The reader of these memoirs will not fail to observe, in addition to ingenuity and perspicuity, much evidence that they were written from a genuine love of inquiry, rather than from the desire for temporary reputation. Although their subjects seem at first not very closely connected, it appears that the later inquiries were suggested by facts developed in the course of those which preceded, and that the author was not looking for subjects on which to write, but was impelled to write by the abundance of material which spontaneously presented itself to his mind. As an incidental result of the optical studies in which he was engaged, he discovered and showed how to correct the peculiar defect of vision now so familiar to oculists under the name of astigmatism, which he found to exist in his own left eye. Probably a considerable number of physicians and of philosophers must have previously been inconvenienced in the same way without undertaking any experiments to discover the exact nature of the hindrance to distinct vision which existed in their cases.

Airy began work as a practical astronomer at a time when what we now understand as practical astronomy was an art as yet, comparatively speaking, unformed, — when much now taught in every text-book had to be discovered or neglected by the observer in proportion to his mental activity or indolence. Neglect was impossible to a mind so active and acute as Airy's ; and while his great contemporary, Bessel, was making the way plain to future practical astronomers, Airy was finding it very successfully for himself. He early recognized and urged the necessity of carefully reducing all observations which are intended to contribute substantially to our knowledge, instead of resting satisfied with the observations themselves. Besides attending thoroughly to all the practical business connected with the management of the Cambridge Observatory, he continued the mathematical investigations which had previously occupied him. Among these should be specially mentioned the memoir on the inequality of long period in the motions of the Earth and Venus, for which the Gold Medal of the Royal Astronomical Society was awarded to him in 1832.

In 1835 Airy received the appointment of Astronomer Royal, and accordingly took charge of the Greenwich Observatory. Here he remained for forty-six years, finding such abundant opportunities for the exercise of his business abilities that his career as an investigator was practically terminated by the acceptance of his new office. New instruments were to be planned, and their construction superintended; new branches of scientific work were to be introduced as part of the regular business of the Observatory; old observations were to be collected, reduced, and published; the methods of making and reducing new observations were to be brought into systematic form; while, in addition to these occupations, demands from other departments of the national administration for advice and assistance in scientific matters were frequently to receive attention from the Astronomer Royal. Substantial progress in any science can only be made by the patient accumulation of observed facts under the guidance of capable administrators, such as Airy. His success in this field of work had to be accepted by himself and by his friends as amends for the withdrawal of his attention from the more strictly scientific problems which he had shown himself so well qualified to solve.

During his administration of the Greenwich Observatory its instrumental equipment was entirely renewed, and in many respects greatly enlarged; magnetic and meteorological observation, and long afterwards spectroscopic observation, were undertaken as parts of the prescribed system of work; the results of older and recent observations were made accessible to the scientific public in a long series of ponderous volumes, to which the astronomical investigators of this century have constantly resorted for an important portion of the facts needed in their studies. No enumeration of the details of Airy's work as Astronomer Royal will be attempted in this place; and as an individual student of nature little remains to be said of him, for the reasons above stated. But his interesting experiments at the Harton Colliery, in 1854, for the determination of the density of the Earth by the observation of pendulums at the surface of the ground and at the bottom of the mine, deserve mention in any notice of his life. In 1870 he began an elaborate investigation into the theory of the Moon's motion, by a new method; but, after pursuing it for many years in such time as was at his command, he found that old age forbade him to carry it further.

He resigned his position as Astronomer Royal in 1881, and lived in honored retirement for the ensuing ten years, dying on January 7, 1892, in consequence of an accidental fall some time before. Marrying in 1830, he became a widower in 1875. Six children survive him. He received the honor of knighthood in 1872, and a long series of other complimentary distinctions at various times in his life.

Besides his original researches, he published, chiefly in his younger days, various essays on scientific matters, distinguished by their accuracy and perspicuity.

WILHELM EDUARD WEBER.

Wilhelm Eduard Weber was born in Wittenberg, October 24, 1804. He was the second of three sons, all of whom became eminent. He was early interested in scientific pursuits, and while yet a student he investigated the phenomena of waves, and with his brother Ernst published a treatise on the subject which has ever since been considered a classic on wave motions. One of the discoveries first made known here was that the particles on the surface of a liquid when there is an advancing wave, all revolve in vertical circles in the plane of the direction of propagation of the wave, while the particles lower down move in ellipses whose vertical axis becomes smaller and smaller as the particles are deeper. This work was issued in 1825, when Weber was but twenty-one years of age. In 1826 he took his doctor's degree at the University of Halle, and was then appointed Privat-docent, and Professor Extraordinary of Physics in 1828.

In 1831 he was called to Göttingen to succeed J. T. Mayer in the Chair of Physics. Here, he with his brother Eduard investigated the mechanism of walking, and this resulted in a treatise on the subject in 1833. This too was a work of high rank. He also published several important papers on acoustics. It will be remembered that it was in these years that Faraday had entered upon his work as a discoverer in electricity and magnetism, and during which he had made known the mechanical relations between magnetism and electricity, and led the way to many devices for utilizing magneto-electric currents. Weber and Gauss were among the first to apply the newly discovered properties to the purposes of telegraphy, and in 1833 they constructed a telegraph connecting the Physical Laboratory of the University with its Observatory, a distance of about three-quarters of a mile. The first use of their devices was to compare the clocks at the two stations, but the line was also used for telegraphic purposes proper. At first only about two letters per minute could be transmitted; nevertheless, in Germany these two are still considered to be the inventors of telegraphy.

In 1837 a new King began his reign in Hanover. His notions of his prerogatives were such that he suspended the constitution, and this called forth vigorous protests from several of the professors at the University, Weber among them. To punish them, seven Professors were dismissed from their chairs, and three were even banished from the country. Weber was thus forced into retirement for some years. In 1843 he was invited to the Chair of Physics at Leipzig, but he returned to his former position in Göttingen in 1849.

The chief contributions to science, those for which he is now best known, and will long continue to be known, are, first, a series of papers beginning in 1846, and continued at intervals to 1864, in which he for the first time showed how the principles of absolute measurement which Gauss had applied to magnetism were applicable to electricity. Until Weber's work there had been no such thing as electrical measurements. There had been nothing more than comparisons between magnitudes of the same kind. Weber showed how an electrical quantity could be stated in terms of the unit of time, length, and mass, without any reference to other electrical phenomena, and this was a new and great achievement. The British Association Committee on Electrical Standards adopted Weber's work as a basis for their standards of units.

Secondly, he was one of the first to feel the necessity for an adequate mechanical conception of electro-magnetic phenomena, and he worked out in a mathematical way, and gave consistency to the idea of molecular magnets, that is, that every molecule of iron is a magnet by constitution, and the various phenomena of the magnetic field are due to the relative positions of these molecules. It hardly needs to be said, that all the known phenomena of magnets, up to date, tend to corroborate and strengthen that conception.

He was an honorary member of many of the learned societies of Europe, as well as of the American Academy.

He died on June 23, 1891, and was therefore eighty-seven years of age.

The names of five persons have been dropped from the list of Resident Fellows on account of removal from the Commonwealth or non-payment of assessments.

The Academy has received an accession of ten Resident Fellows, and two Associate Fellows.

The Roll of the Academy, corrected to date, includes the names of 176 Fellows, 87 Associate Fellows, and 65 Foreign Honorary Members.

May 24, 1892.

LIST

OF THE

FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to March, 1893.)

RESIDENT FELLOWS. — 191.

(Number limited to two hundred.)

Class I. — *Mathematical and Physical Sciences.* — 70.

Section I. — 7.

Mathematics.

Benj. A. Gould,	Cambridge.
Gustavus Hay,	Boston.
Benjamin O. Peirce,	Cambridge.
John D. Runkle,	Brookline.
T. H. Safford,	Williamstown.
William E. Story,	Worcester.
Henry Taber,	Worcester.

Section II. — 10.

Practical Astronomy and Geodesy.

Solon I. Bailey,	Cambridge.
Seth C. Chandler,	Cambridge.
Alvan G. Clark,	Cambridgeport.
J. Rayner Edmands.	Cambridge.
Henry Mitchell,	Boston.
Edward C. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
O. C. Wendell,	Cambridge.

Section III. — 41.

Physics and Chemistry.

A. Graham Bell,	Washington.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Arthur M. Comey,	Somerville.
Josiah P. Cooke,	Cambridge.
Charles R. Cross,	Boston.
Amos E. Dolbear,	Somerville.
Thos. M. Drown,	Boston.
Charles W. Eliot,	Cambridge.
Moses G. Farmer,	Eliot, Me.
Thomas Gaffield,	Boston.
Wolcott Gibbs,	Newport, R. I.
Edwin H. Hall,	Cambridge.
Henry B. Hill,	Cambridge.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
Henry M. Howe,	Boston.
Charles L. Jackson,	Cambridge.
William W. Jacques,	Newton.
Alonzo S. Kimball,	Worcester.
Leonard P. Kinnicutt,	Worcester.

William R. Livermore,	Boston.
Charles F. Mabery,	Cleveland.
A. A. Michelson,	Worcester.
George D. Moore,	Worcester.
Charles E. Munroe,	Washington.
John U. Nef,	Chicago, Ill.
Lewis M. Norton,	Newton.
Robert H. Richards,	Boston.
Theodore W. Richards,	Cambridge.
Edward S. Ritchie,	Newton.
A. Lawrence Rotch,	Boston.
Charles R. Sanger,	Cambridge.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Elihu Thomson,	Lynn.
John Trowbridge,	Cambridge.
Harold Whiting,	Cambridge.
Charles H. Wing,	Ledger, N. C.
Edward S. Wood,	Cambridge.

SECTION IV. — 12.

Technology and Engineering.

Eliot C. Clarke,	Boston.
Gaetano Lanza,	Boston.
E. D. Leavitt,	Cambridgeport.
Hiram F. Mills,	Lawrence.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Boston.
Andrew H. Russell,	Boston.
Peter Schwamb,	Arlington.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

CLASS II. — *Natural and Physiological Sciences.* — 57.

SECTION I. — 9.

Geology, Mineralogy, and Physics of the Globe.

Thomas T. Bouvé,	Boston.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
O. W. Huntington,	Cambridge.
Jules Marcou,	Cambridge.
William H. Niles,	Cambridge.
Nathaniel S. Shaler,	Cambridge.
Warren Upham,	Somerville.

SECTION II. — 9.

Botany.

William G. Farlow,	Cambridge.
Charles E. Faxon,	Boston.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
Benj. L. Robinson,	Cambridge.
Charles S. Sargent,	Brookline.
Arthur B. Seymour,	Cambridge.
Charles J. Sprague,	Boston.
Roland Thaxter,	Cambridge.

SECTION III. — 20.

Zoölogy and Physiology.

Alex. E. R. Agassiz,	Cambridge.
Robert Amory,	Boston.
James M. Barnard,	Milton.
Henry P. Bowditch,	Boston.
Wm. Brewster,	Cambridge.
Louis Cabot,	Brookline.
Harold C. Ernst,	Boston.
J. Walter Fewkes,	Boston.
Edw. G. Gardiner,	Boston.
Samuel Henshaw,	Cambridge.
Alpheus Hyatt,	Cambridge.
Theodore Lyman,	Brookline.
Edward L. Mark,	Cambridge.
Charles S. Minot,	Boston.
Edward S. Morse,	Salem.
James J. Putnam,	Boston.
Samuel H. Scudder,	Cambridge.
William T. Sedgwick,	Boston.
Henry Wheatland,	Salem.
James C. White,	Boston.

SECTION IV. — 19.

Medicine and Surgery.

Samuel L. Abbot,	Boston.
Edward H. Bradford,	Boston.
Arthur T. Cabot,	Boston.
David W. Cheever,	Boston.
Benjamin E. Cotting,	Roxbury.
Frank W. Draper,	Boston.
Thomas Dwight,	Boston.
Reginald H. Fitz,	Boston.
Charles F. Folsom,	Boston.
Richard M. Hodges,	Boston.
Oliver W. Holmes,	Boston.
Frederick I. Knight,	Boston.
Francis Minot,	Boston.
Samuel J. Mixter,	Boston.
Wm. L. Richardson,	Boston.
George C. Shattuck,	Boston.
Henry P. Walcott,	Cambridge.
John C. Warren,	Boston.
Henry W. Williams,	Boston.

CLASS III. — *Moral and Political Sciences.* — 64.

SECTION I. — 10.

Philosophy and Jurisprudence.

James B. Ames,	Cambridge.
Charles C. Everett,	Cambridge.
Horace Gray,	Boston.
John C. Gray,	Boston.
Nathaniel Holmes,	Cambridge.
John E. Hudson,	Boston.
John Lowell,	Newton.
Henry W. Paine,	Cambridge.
Josiah Royce,	Cambridge.
James B. Thayer,	Cambridge.

SECTION II. — 19.

Philology and Archæology.

William S. Appleton,	Boston.
Charles P. Bowditch,	Boston.
Lucien Carr,	Cambridge.
Franklin Carter,	Williamstown.
Joseph T. Clarke,	Boston.
Henry G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Henry W. Haynes,	Boston.
Bennett H. Nash,	Boston.
Frederick W. Putnam,	Cambridge.
Edward Robinson,	Boston.
F. B. Stephenson,	Boston.
Joseph H. Thayer,	Cambridge.
Crawford H. Toy,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
Edward J. Young,	Waltham.

SECTION III. — 23.

Political Economy and History.

Charles F. Adams,	Quincy.
Edward Atkinson,	Boston.
Edmund H. Bennett,	Boston.
Mellen Chamberlain,	Chelsea.
John Cummings,	Woburn.
Andrew M. Davis,	Cambridge.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
Ephraim Emerton,	Cambridge.
A. C. Goodell, Jr.,	Salem.
Henry C. Lodge,	Boston.
Augustus Lowell,	Boston.
Edward J. Lowell,	Boston.
Silas M. Macvane,	Cambridge.
Francis Parkman,	Boston.
Andrew P. Peabody,	Cambridge.
John C. Ropes,	Boston.
Denman W. Ross,	Cambridge.
Charles C. Smith,	Boston.
F. W. Taussig,	Cambridge.
Henry W. Torrey,	Cambridge.
Francis A. Walker,	Boston.
Robert C. Winthrop,	Boston.

SECTION IV.—12.

Literature and the Fine Arts.

Francis Bartlett,	Boston.
John Bartlett,	Cambridge.
George S. Boutwell,	Groton.
Martin Brimmer,	Boston.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
Thos. W. Higginson,	Cambridge.
Charles G. Loring,	Boston.
Percival Lowell,	Brookline.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.

ASSOCIATE FELLOWS.—96.

(Number limited to one hundred.)

CLASS I.—*Mathematical and Physical Sciences.*—36.

SECTION I.—6.

Mathematics.

Fabian Franklin,	Baltimore.
Emory McClintock,	New York.
Simon Newcomb,	Washington.
H. A. Newton,	New Haven.
James E. Oliver,	Ithaca, N.Y.
J. N. Stockwell,	Cleveland, Ohio.

SECTION II.—14.

Practical Astronomy and Geodesy.

Edward E. Barnard,	San José, Cal.
W. H. C. Bartlett,	Yonkers, N.Y.
S. W. Burnham,	Chicago.
Geo. Davidson,	San Francisco.
Wm. H. Emory,	Washington.
Asaph Hall,	Washington.
George W. Hill,	Washington.
E. S. Holden,	San José, Cal.
James E. Keeler,	Allegany, Pa.
Sam. P. Langley,	Washington.
T. C. Mendenhall,	Washington.
William A. Rogers,	Waterville, Me.
George M. Searle,	Washington.
Chas. A. Young,	Princeton, N.J.

SECTION III.—11.

Physics and Chemistry.

Carl Barus,	Washington.
J. Willard Gibbs,	New Haven.
Frank A. Gooch,	New Haven.
S. W. Johnson,	New Haven.
M. C. Lea,	Philadelphia.
J. W. Mallet,	Charlottesville, Va.
A. M. Mayer,	Hoboken, N. J.
Edward W. Morley,	Cleveland, O.
Ira Remsen,	Baltimore.
Ogden N. Rood,	New York.
H. A. Rowland,	Baltimore.

SECTION IV.—5.

Technology and Engineering.

Henry L. Abbot,	New York.
Cyrus B. Comstock,	Washington.
Geo. S. Morison,	New York.
John Newton,	New York.
William Sellers,	Philadelphia.

CLASS II.—*Natural and Physiological Sciences.*—31.

SECTION I.—14.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
James D. Dana,	New Haven.
Sir J. W. Dawson,	Montreal.
F. A. Genth,	Philadelphia.
James Hall,	Albany, N.Y.
F. S. Holmes,	Charleston, S.C.
Clarence King,	New York.
Joseph Le Conte,	Berkeley, Cal.
J. Peter Lesley,	Philadelphia.
J. W. Powell,	Washington.
R. Pumpelly,	Newport, R.I.
Alfred R. C. Selwyn,	Ottawa.
Geo. C. Swallow,	Columbia, Mo.

SECTION II. — 4.

Botany.

A. W. Chapman,	Apalachicola, Fla.
D. C. Eaton,	New Haven.
Wm. Trelease,	St. Louis.
George Vasey,	Washington.

SECTION III. — 8.

Zoölogy and Physiology.

Joel A. Allen,	New York.
Wm. K. Brooks,	Baltimore.
George B. Goode,	Washington.
O. C. Marsh,	New Haven.
H. N. Martin,	Baltimore.
S. Weir Mitchell,	Philadelphia.
A. S. Packard,	Providence.
A. E. Verrill,	New Haven.

SECTION IV. — 5.

Medicine and Surgery.

John S. Billings,	Washington.
Jacob M. Da Costa,	Philadelphia.
W. A. Hammond,	New York.
Alfred Stillé,	Philadelphia.
H. C. Wood,	Philadelphia.

CLASS III. — *Moral and Political Sciences.* — 29.

SECTION I. — 8.

Philosophy and Jurisprudence.

T. M. Cooley,	Ann Arbor, Mich.
D. R. Goodwin,	Philadelphia.
A. G. Haygood,	Oxford, Ga.
James McCosh,	Princeton, N.J.
Charles S. Peirce,	New York.
Thos. R. Pynchon,	Hartford, Conn.
E. G. Robinson,	Providence.
Jeremiah Smith,	Dover, N. H.

SECTION II. — 7.

Philology and Archæology.

A. N. Arnold,	Pawtuxet, R.I.
Timothy Dwight,	New Haven.
D. C. Gilman,	Baltimore.
A. C. Kendrick,	Rochester, N.Y.
E. E. Salisbury,	New Haven.
A. D. White,	Ithaca, N.Y.
W. D. Whitney,	New Haven.

SECTION III. — 8.

Political Economy and History.

Henry Adams,	Washington.
Geo. P. Fisher,	New Haven.
M. F. Force,	Cincinnati.
Henry C. Lea,	Philadelphia.
Edward J. Phelps,	Burlington, Vt.
W. G. Sumner,	New Haven.
J. H. Trumbull,	Hartford, Conn.
David A. Wells,	Norwich, Conn.

SECTION IV. — 6.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich.
L. P. di Cesnola,	New York.
F. E. Church,	New York.
R. S. Greenough,	Florence.
William W. Story,	Rome.
Wm. R. Ware,	New York.

FOREIGN HONORARY MEMBERS.—69.

(Elected as vacancies occur.)

Class I.—*Mathematical and Physical Sciences.*—24.

Section I.—5.

Mathematics.

Francesco Brioschi,	Milan.
Arthur Cayley,	Cambridge.
Hugo Gyldén,	Stockholm.
Charles Hermite,	Paris.
J. J. Sylvester,	Oxford.

Section II.—6.

Practical Astronomy and Geodesy.

Arthur Auwers,	Berlin.
J. H. W. Döllen,	Pulkowa.
H. A. E. A. Faye,	Paris.
William Huggins,	London.
Otto Struve,	Pulkowa.
H. C. Vogel,	Potsdam.

Section III.—11.

Physics and Chemistry.

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
R. Bunsen,	Heidelberg.
H. L. F. Helmholtz,	Berlin.
Mendeleeff,	St. Petersburg.
Victor Meyer,	Heidelberg.
Marignac,	Geneva.
Lord Rayleigh,	Witham.
Sir H. E. Roscoe,	London.
Sir G. G. Stokes,	Cambridge.
Julius Thomsen,	Copenhagen.

Section IV.—2.

Technology and Engineering.

Lord Kelvin,	Glasgow.
F. M. de Lesseps,	Paris.

Class II.—*Natural and Physiological Sciences.*—25.

Section I.—6.

Geology, Mineralogy, and Physics of the Globe.

H. Ernst Beyrich,	Berlin.
Alfred Des Cloizeaux,	Paris.
A. E. Nordenskiöld,	Stockholm.
C. F. Rammelsberg,	Berlin.
Henry C. Sorby,	Sheffield.
Heinrich Wild,	St. Petersburg.

Section II.—7.

Botany.

J. G. Agardh.	Lund.
Alphonse de Candolle,	Geneva.
Sir Joseph D. Hooker,	London.
Baron von Mueller,	Melbourne.
Julius Sachs,	Würzburg.
Marquis de Saporta,	Aix.
Eduard Strasburger,	Bonn.

Section III. — 9.

Zoölogy and Physiology.

P. J. Van Beneden,	Louvain.
Du Bois-Reymond,	Berlin.
Thomas H. Huxley,	London.
Albrecht Kölliker,	Würzburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
C. F. W. Ludwig,	Leipsic.
Louis Pasteur,	Paris.
J. J. S. Steenstrup,	Copenhagen

Section IV. — 3.

Medicine and Surgery.

C. E. Brown-Séquard,	Paris.
Sir James Paget,	London.
Rudolph Virchow,	Berlin.

Class III. — *Moral and Political Sciences.* — 20.

Section I. — 3.

Philosophy and Jurisprudence.

James Martineau,	London.
Henry Sidgwick,	Cambridge.
Sir James F. Stephen,	London.

Section II. — 7.

Philology and Archæology.

Sir John Evans,	Hemel Hempstead.
Pascual de Gayangos,	Madrid.
Benjamin Jowett,	Oxford.
J. W. A. Kirchhoff,	Berlin.
G. C. C. Maspero,	Paris.
Max Müller,	Oxford.
Sir H. C. Rawlinson,	London.

Section III. — 7.

Political Economy and History.

Duc de Broglie,	Paris.
Ernst Curtius,	Berlin.
W. Ewart Gladstone,	Hawarden.
Charles Merivale,	Ely.
Theodor Mommsen,	Berlin.
Jules Simon,	Paris.
Wm. Stubbs,	Oxford.

Section IV. — 3.

Literature and the Fine Arts.

Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Leslie Stephen,	London.

STATUTES AND STANDING VOTES.

STATUTES.

(*Adopted May* 30, 1854 : *amended September* 8, 1857, *November* 12, 1862, *May* 24, 1864, *November* 9, 1870, *May* 27, 1873, *January* 26, 1876, *June* 16, 1886, *October* 8, 1890, *and January* 11, 1893.)

CHAPTER I.

OF FELLOWS AND FOREIGN HONORARY MEMBERS.

1. The Academy consists of *Fellows* and *Foreign Honorary Members*. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, viz.: Class I. The Mathematical and Physical Sciences; — Class II. The Natural and Physiological Sciences; — Class III. The Moral and Political Sciences. Each Class is divided into four Sections, viz.: Class I., Section 1. Mathematics; — Section 2. Practical Astronomy and Geodesy; — Section 3. Physics and Chemistry; — Section 4. Technology and Engineering. Class II., Section 1. Geology, Mineralogy, and Physics of the Globe; — Section 2. Botany; — Section 3. Zoölogy and Physiology; — Section 4. Medicine and Surgery. Class III., Section 1. Philosophy and Jurisprudence; — Section 2. Philology and Archæology; — Section 3. Political Economy and History; — Section 4. Literature and the Fine Arts.

2. Fellows, resident in the State of Massachusetts, only, may vote at the meetings of the Academy.* Each Resident Fellow shall pay an admission fee of ten dollars and such annual assessment, not exceeding ten dollars, as shall be voted by the Academy at each annual meeting.

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* The number of Resident Fellows is limited by the Charter to 200.

3. Fellows residing out of the State of Massachusetts shall be known and distinguished as Associate Fellows. They shall not be liable to the payment of any fees or annual dues, but on removing within the State shall be admitted to the privileges,* and be subject to the obligations, of Resident Fellows. The number of Associate Fellows shall not exceed *one hundred*, of whom there shall not be more than *forty* in either of the three Classes of the Academy.

4. The number of Foreign Honorary Members shall not exceed *seventy-five;* and they shall be chosen from among persons most eminent in foreign countries for their discoveries and attainments in either of the three departments of knowledge above enumerated. And there shall not be more than *thirty* Foreign Members in either of these departments.

CHAPTER II.

OF OFFICERS.

1. There shall be a President, a Vice-President, a Corresponding Secretary, a Recording Secretary, a Treasurer, and a Librarian, which officers shall be annually elected, by written votes, at the Annual Meeting, on the day next preceding the last Wednesday in May.

2. At the same time, and in the same manner, nine Councillors shall be elected, three from each Class of the Academy, but the same Fellows shall not be eligible on more than three successive years. These nine Councillors, with the President, Vice-President, the two Secretaries, the Treasurer, and the Librarian, shall constitute the Council. It shall be the duty of this Council to exercise a discreet supervision over all nominations and elections. With the consent of the Fellow interested, they shall have power to make transfers between the several Sections of the same Class, reporting their action to the Academy.

3. If any office shall become vacant during the year, the vacancy shall be filled by a new election, and at the next stated meeting.

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* Associate Fellows may attend, but cannot vote, at meetings of the Academy. See Chapter I., 2.

CHAPTER III.

OF THE PRESIDENT.

1. It shall be the duty of the President, and, in his absence, of the Vice-President, or next officer in order as above enumerated, to preside at the meetings of the Academy; to summon extraordinary meetings, upon any urgent occasion; and to execute or see to the execution of the Statutes of the Academy.

2. The President, or, in his absence, the next officer as above enumerated, is empowered to draw upon the Treasurer for such sums of money as the Academy shall direct. Bills presented on account of the Library, or the Publications of the Academy, must be previously approved by the respective committees on these departments.

3. The President, or, in his absence, the next officer as above enumerated, shall nominate members to serve on the different committees of the Academy which are not chosen by ballot.

4. Any deed or writing to which the common seal is to be affixed shall be signed and sealed by the President, when thereto authorized by the Academy.

CHAPTER IV.

OF STANDING COMMITTEES.

1. At the Annual Meeting there shall be chosen the following Standing Committees, to serve for the year ensuing, viz.: —

2. The Committee of Finance, to consist of the President, Treasurer, and one Fellow chosen by ballot, who shall have charge of the investment and management of the funds and trusts of the Academy. The general appropriations for the expenditures of the Academy shall be moved by this Committee at the Annual Meeting, and all special appropriations from the general and publication funds shall be referred to or proposed by this Committee.

3. The Rumford Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications and claims for the Rumford Premium, also on all appropriations from the income of the Rumford Fund, and generally see to the due and proper execution of this trust.

4. The Committee of Publication, of three Fellows, to whom all

memoirs submitted to the Academy shall be referred, and to whom the printing of memoirs accepted for publication shall be intrusted.

5. The Committee on the Library, of three Fellows, who shall examine the Library, and make an annual report on its condition and management.

6. An Auditing Committee, of two Fellows, for auditing the accounts of the Treasurer.

CHAPTER V.

OF THE SECRETARIES.

1. The Corresponding Secretary shall conduct the correspondence of the Academy, recording or making an entry of all letters written in its name, and preserving on file all letters which are received; and at each meeting he shall present the letters which have been addressed to the Academy since the last meeting. With the advice and consent of the President, he may effect exchanges with other scientific associations, and also distribute copies of the publications of the Academy among the Associate Fellows and Foreign Honorary Members, as shall be deemed expedient; making a report of his proceedings at the Annual Meeting. Under the direction of the Council for Nomination, he shall keep a list of the Fellows, Associate Fellows, and Foreign Honorary Members, arranged in their Classes and in Sections in respect to the special sciences in which they are severally proficient; and he shall act as secretary to the Council.

2. The Recording Secretary shall have charge of the Charter and Statute-book, journals, and all literary papers belonging to the Academy. He shall record the proceedings of the Academy at its meetings; and after each meeting is duly opened, he shall read the record of the preceding meeting. He shall notify the meetings of the Academy, and apprise committees of their appointment. He shall post up in the Hall a list of the persons nominated for election into the Academy; and when any individual is chosen, he shall insert in the record the names of the Fellows by whom he was nominated.

3. The two Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the proceedings of the Academy as may seem to them calculated to promote the interests of science.

CHAPTER VI.

OF THE TREASURER.

1. The Treasurer shall give such security for the trust reposed in him as the Academy shall require.

2. He shall receive officially all moneys due or payable, and all bequests or donations made to the Academy, and by order of the President or presiding officer shall pay such sums as the Academy may direct. He shall keep an account of all receipts and expenditures; shall submit his accounts to the Auditing Committee; and shall report the same at the expiration of his term of office.

3. The Treasurer shall keep a separate account of the income and appropriation of the Rumford Fund, and report the same annually.

4. All moneys which there shall not be present occasion to expend shall be invested by the Treasurer, under the direction of the Finance Committee, on such securities as the Academy shall direct.

CHAPTER VII.

OF THE LIBRARIAN AND LIBRARY.

1. It shall be the duty of the Librarian to take charge of the books, to keep a correct catalogue of the same, and to provide for the delivery of books from the Library. He shall also have the custody of the publications of the Academy.

2. The Librarian, in conjunction with the Committee on the Library, shall have authority to expend, as they may deem expedient, such sums as may be appropriated, either from the Rumford or the General Fund of the Academy, for the purchase of books, and for defraying other necessary expenses connected with the Library. They shall have authority to propose rules and regulations concerning the circulation, return, and safe-keeping of books; and to appoint such agents for these purposes as they may think necessary.

3. To all books in the Library procured from the income of the Rumford Fund, the Librarian shall cause a stamp or label to be affixed, expressing the fact that they were so procured.

4. Every person who takes a book from the Library shall give a receipt for the same to the Librarian or his assistant.

5. Every book shall be returned in good order, regard being had to the necessary wear of the book with good usage. And if any book shall be lost or injured, the person to whom it stands charged shall replace it by a new volume or set, if it belongs to a set, or pay the current price of the volume or set to the Librarian; and thereupon the remainder of the set, if the volume belonged to a set, shall be delivered to the person so paying for the same.

6. All books shall be returned to the Library for examination, at least one week before the Annual Meeting.

CHAPTER VIII.

Of Meetings.

1. There shall be annually four stated meetings of the Academy; namely, on the second Wednesday in May (the Annual Meeting), on the second Wednesday in October, on the second Wednesday in January, and on the second Wednesday in March; to be held in the Hall of the Academy, in Boston. At these meetings only, or at meetings adjourned from these and regularly notified, shall appropriations of money be made, or alterations of the statutes or standing votes of the Academy be effected.

2. Fifteen Fellows shall constitute a quorum for the transaction of business at a stated meeting. Seven Fellows shall be sufficient to constitute a meeting for scientific communications and discussions.

3. The Recording Secretary shall notify the meetings of the Academy to each Fellow residing in Boston and the vicinity; and he may cause the meetings to be advertised, whenever he deems such further notice to be needful.

CHAPTER IX.

Of the Election of Fellows and Honorary Members.

1. Elections shall be made by ballot, and only at stated meetings.

2. Candidates for election as Resident Fellows must be proposed by two or more Resident Fellows, in a recommendation signed by

them, specifying the Section to which the nomination is made, which recommendation shall be transmitted to the Corresponding Secretary, and by him referred to the Council for Nomination. No person recommended shall be reported by the Council as a candidate for election, unless he shall have received a written approval, signed at a meeting of the Council by at least eight of its members. All nominations thus approved shall be read to the Academy at a stated meeting, and shall then stand on the nomination list during the interval between two stated meetings, and until the balloting. No person shall be elected a Resident Fellow, unless he shall have been resident in this Commonwealth one year next preceding his election; and any Resident Fellow who shall remove his domicile from the Commonwealth, shall be deemed to have abandoned his Fellowship. If any person elected a Resident Fellow shall neglect for one year to pay his admission fee, his election shall be void; and, if any Resident Fellow shall neglect to pay his annual assessments for two years, provided that his attention shall have been called to this article, he shall be deemed to have abandoned his Fellowship; but it shall be in the power of the Treasurer, with the consent of the Council, to dispense (*sub silentio*) with the payment both of the admission fee and of the assessments, whenever in any special instance he shall think it advisable so to do.

3. The nomination of Associate Fellows shall take place in the manner prescribed in reference to Resident Fellows; and after such nomination shall have been publicly read at a stated meeting previous to that when the balloting takes place, it shall be referred to a Council for Nomination; and a written approval, authorized and signed at a meeting of said Council by at least seven of its members, shall be requisite to entitle the candidate to be balloted for. The Council may in like manner originate nominations of Associate Fellows, which must be read at a stated meeting previous to the election, and be exposed on the nomination list during the interval.

4. Foreign Honorary Members shall be chosen only after a nomination made at a meeting of the Council, signed at the time by at least seven of its members, and read at a stated meeting previous to that on which the balloting takes place.

5. Three fourths of the ballots cast must be affirmative, and the number of affirmative ballots must amount to eleven to effect an election of Fellows or Foreign Honorary Members.

6. Each section of the Academy is empowered to present lists of persons deemed best qualified to fill vacancies occurring in the

number of Foreign Honorary Members or Associate Fellows allotted to it; and such lists, after being read at a stated meeting, shall be referred to the Council for Nomination.

7. If, in the opinion of a majority of the entire Council, any Fellow — Resident or Associate — shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his Fellowship; and, provided that a majority of two thirds of the Fellows at a stated meeting, consisting of not less than fifty Fellows, shall adopt this recommendation, his name shall be stricken off the roll of Fellows.

CHAPTER X.

Of Amendments of the Statutes.

1. All proposed alterations of the Statutes, or additions to them, shall be referred to a committee, and, on their report at a subsequent meeting, shall require for enactment a majority of two thirds of the members present, and at least eighteen affirmative votes.

2. Standing Votes may be passed, amended, or rescinded, at any stated meeting, by a majority of two thirds of the members present. They may be suspended by a unanimous vote.

CHAPTER XI.

Of Literary Performances.

1. The Academy will not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its publications.

STANDING VOTES.

1. Communications of which notice has been given to the Secretary shall take precedence of those not so notified.

2. Resident Fellows who have paid all fees and dues chargeable to them are entitled to receive one copy of each volume or article printed by the Academy, on application to the Librarian personally or by written order, within two years from the date of publication. And the current issues of the Proceedings shall be supplied, when ready for publication, free of charge to all the Fellows and Members of the Academy who desire to receive them.

3. The Committee of Publication shall fix from time to time the price at which the publications of the Academy may be sold. But members may be supplied at half this price with volumes which they are not entitled to receive free, and which are needed to complete their sets.

4. Two hundred extra copies of each paper accepted for publication in the Memoirs or Proceedings of the Academy shall be placed at the disposal of the author, free of charge.

5. Resident Fellows may borrow and have out from the Library six volumes at any one time, and may retain the same for three months, and no longer.

6. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.

7. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy, except by special leave of the Librarian.

8. Books, publications, or apparatus shall be procured from the income of the Rumford Fund only on the certificate of the Rumford Committee, that they, in their opinion, will best facilitate and encourage the making of discoveries and improvements which may merit the Rumford Premium.

9. The annual meeting and the other stated meetings shall be holden at eight o'clock, P. M.

10. A meeting for receiving and discussing scientific communications may be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September.

RUMFORD PREMIUM.

In conformity with the terms of the gift of Benjamin, Count Rumford, granting a certain fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of said fund, as it now exists, at any annual meeting, an award of a gold and silver medal, being together of the intrinsic value of three hundred dollars, as a premium to the author of any important discovery or useful improvement in light or in heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands; preference being always given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind; and to add to such medals, as a further premium for such discovery and improvement, if the Academy see fit so to do, a sum of money not exceeding three hundred dollars.

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